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DEVELOPMENT OF DESIGN CRITERIA FOR AN ELECTROCHEMICAL WATER RECLAMATION SYSTEM

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DEVELOPMENT OF DESIGN CRITERIA FOR AN ELECTROCHEMICAL WATER RECLAMATION SYSTEM

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SUMMARY

An experimental program was conducted to develop design criteria for an electrochemical system that will recover usable water from urine with a minimum requirement for power and expendable supplies. This report presents the results of the program which consisted of the following efforts:

1. A basic examination of the electrochemical pretreatment process for removing the organic constituents from urine using Astropower catalysts.
2. Combining an optimized electrochemical pretreatment stage with the process of electrodialysis as a system for recovering the water in urine.
3. Identifying criteria and problems to form the basis for the design of a flight-concept prototype, integrated, electrochemical reclamation system.

The major effort was devoted to a study of the urine electrochemical pretreatment process. This study culminated with the construction and testing of an electrolytic pretreatment cell capable of processing nine pounds of urine in less than 16.5 hours and requiring 170 watthours per pound of urine to remove over 97% of the Total Kjeldahl Nitrogen content from normal urine. No research or development effort was given to the electrodialysis process. A five-consecutive-day water reclamation test with a combined system consisting of this electrolytic pretreatment cell and an electrodialysis stack resulted in demonstrating that this system was capable of processing nine pounds of urine in less than 16 hours and requiring less than 200 watthours per pound of product water to produce a water containing less than 500 ppm dissolved solids. Cultures prepared from samples of pretreated urine indicated the absence of bacteria. No degradation of cell components or performance was detected.

INTRODUCTION

The objective of this experimental program was to develop design criteria for an electrochemical system that will recover usable water from urine on medium-to-long-term space missions, with a minimum requirement for power and expendable supplies.

In developing the design criteria, the following ultimate design objectives were considered:

1. four man continuous operation for a duration of two years,
2. zero g operation,
3. trade-off studies to optimize weight, power, and expendables using a power penalty of 350 pounds per kilowatt of electrical power required,
4. expendable requirements of less than 0.4 percent by weight of the water recovered,
5. less than 500 ppm dissolved solids in product water (250 ppm is preferred),
6. complete, integrated, electrochemical urine water reclamation system, operating at significantly less than 315 watt-hours per pound of water recovered (state-of-the-art is 300 watt-hours/pound for electrolytic pretreatment and 15 watt-hours/pound for electrodialysis),
7. an overall recovery efficiency, defined as percent of available water recovered from electrolyzed input, of at least 92 percent (considered state-of-the-art).

A continuing effort has been made by the National Aeronautics and Space Administration to investigate different water reclamation concepts for defining the more promising systems and improvements in the state-of-the-art. The practicality of several of the more promising systems depends upon effective pretreatment techniques to remove urea and other organics from the raw urine (see ref. 1). A major problem with the reclamation of water in urine is the presence of urea and other nitrogen-containing compounds. These constituents make raw urine an excellent nutrient media for bacterial growth and they are susceptible to bacterial and thermal decomposition liberating quantities of ammonia. Organic solutes must also be removed from electrodialysis feed to prevent membrane fouling.

One of the most promising effective pretreatment techniques involves an electrochemical oxidation process that decomposes urea and other organics into hydrogen, nitrogen, and carbon dioxide gases.

The oxidation of urea can proceed by the intermediate electrochemical formation of sodium hypochlorite. Generation of sufficient hypochlorite fixes the current consumption at 6 Faradays (F) per mole of urea as shown in the following equations.

Anode: $$6Cl^- - 6e \rightarrow 3Cl_2 \quad (1)$$

Cathode: $$6Na^+ + 6HOH + 6e \rightarrow 6NaOH + 3H_2 \quad (2)$$

Mixing: $$6NaOH + 3Cl_2 \rightarrow 3NaO\,Cl + 3NaCl + 3H_2O \quad (3)$$

Oxidation: $CO(NH_2)_2 + 3NaO\,Cl \rightarrow CO_2 + N_2 + 3NaCl + 2H_2O$ (4)

Overall Reaction: $CO(NH_2)_2 + H_2O \rightarrow CO_2 + N_2 + 3H_2$ (5)

Research initiated by NASA on the electrolysis pretreatment technique revealed that this process was feasible, that the technique needed additional study to optimize the energy requirement and accelerate the processing time, and that a combined system involving subsequent water reclamation was required for a complete evaluation (see ref. 2 and 3). Further research for NASA in the development of a urine-water reclamation system combining the techniques of electrolytic pretreatment and reverse osmosis resulted in the fabrication of a system that produced recovered water containing 9700 ppm of total dissolved solids at an overall recovery that consumed at least 210 watt-hours of energy per pound of water recovered (see ref. 4)

A company-funded research program at Astropower Laboratory developed a catalyst that accelerated the rate of electrochemical oxidation of urea and reduced the power requirement when compared with the uncatalyzed process. Further research was conducted in this study on the improved catalytic electrochemical oxidation process. Research was conducted to:

1. optimize the electrolytic treatment of urine by laboratory tests using specially designed laboratory electrolysis cells,
2. identify the problems that may be encountered in an electrodialysis unit when it is operated on the effluent from an electrolytic pretreatment cell (operating on urine) and devise means for making the combination of electrochemical systems more conservative of energy and more reliable,
3. establish (basic data on the properties of urine at various concentrations and) experimental data that will form the basis for the design of a flight concept prototype electrochemical reclamation system employing the principles of electrolytic pretreatment and electrodialysis.

ELECTROCHEMICAL EXPERIMENTS

This section contains a description and discussion of laboratory apparatus constructed for this study. Each apparatus described was used to study a particular facet or set of variables of the process. Experimentation with the electrochemical cells also provided valuable information for scaling to a larger size. Thus by progressing to larger cells, not only were the effects of the process variables elucidated, but engineering and scaling factors began to assume more important considerations. This study resulted in the construction and operation of the Mark III cell which was able to treat in excess of nine pounds of urine per day.

This section also contains a description of the procedure of cell operation, the analytical procedures used and the method of data handling and reduction.

Design and Fabrication of Laboratory Apparatus

Catalyst screening apparatus. — The effect of various oxidation catalysts on the reaction between sodium hypochlorite and the organic constituents of urine was evaluated using the apparatus shown in Figure 1. This apparatus was a sealed system from which air could be excluded and consisted of a 1000-ml reaction flask connected to a gas measuring system. The reaction flask was equipped with magnetic stirring, a thermometer, an addition funnel and helium purging lines. The gas measuring system was equipped with absorption devices for collecting water vapor and carbon dioxide, a rubber septum for taking gas analysis samples, and a wet test meter for measuring the volume of gas evolved from the reaction.

Each catalyst was dissolved completely in the urine for 15 minutes before the hypochlorite was added. During this same period of time, the complete reaction apparatus was purged with helium to the point where the nitrogen measured less than 0.1 percent by volume. A Beckman, model GC-2A, gas chromatograph with a type 13X molecular sieve column was used to measure gas compositions. The ultraviolet light source was a PCQ9G-1 quartz lamp and was obtained from Ultra Violet Products, Inc. Mercury was used as an internal photosensitizer.

Mark I cell. — The Mark I laboratory electrolysis cell shown in Figure 2 was designed and fabricated so that urine would flow in one pass through the cell in the electrode spacing between a stack of alternate anodes and cathodes. This design permits the cell to be used in the loop of a continuously circulating urine flow system; this appeared to offer the most flexibility in operation. This system also appeared to offer the highest probability of reproducing the same constant operating conditions for different test runs.

The electrode stacks consisted of 10, 14 or 16 platinum sheets with total electrode areas of 407.9, 589.2 and 679.8 cm^2, respectively, and electrode spacings of 0.062, 0.048 and 0.042 inch between each alternate anode and cathode. Each platinum electrode was approximately 0.005 inch thick, 4 cm

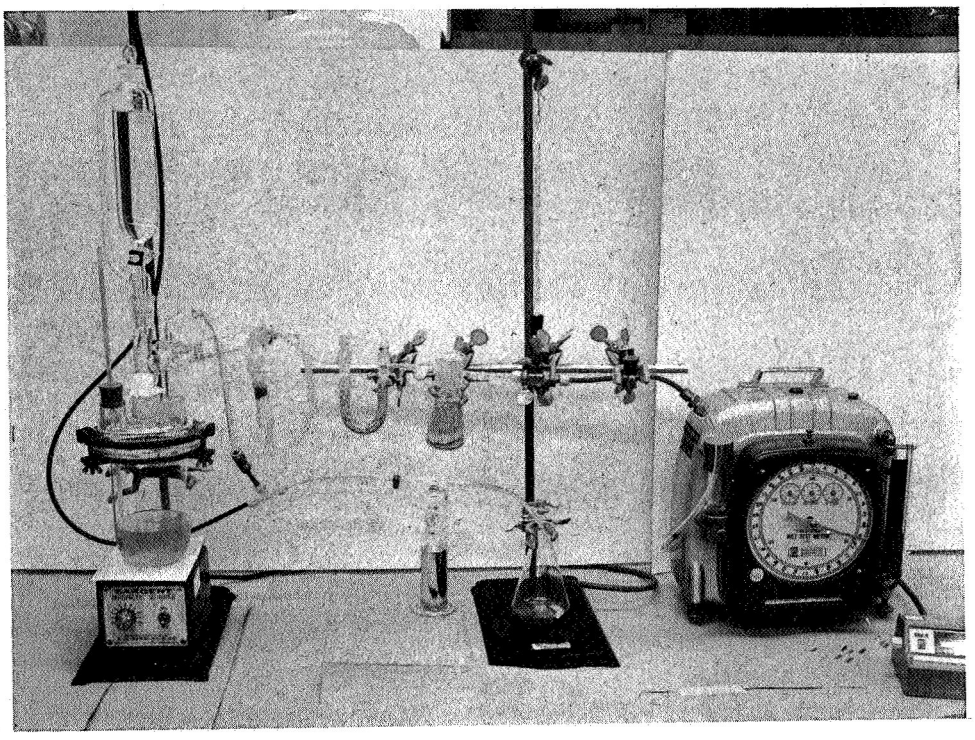

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Figure 1. Apparatus for Hypochlorite Oxidation Studies

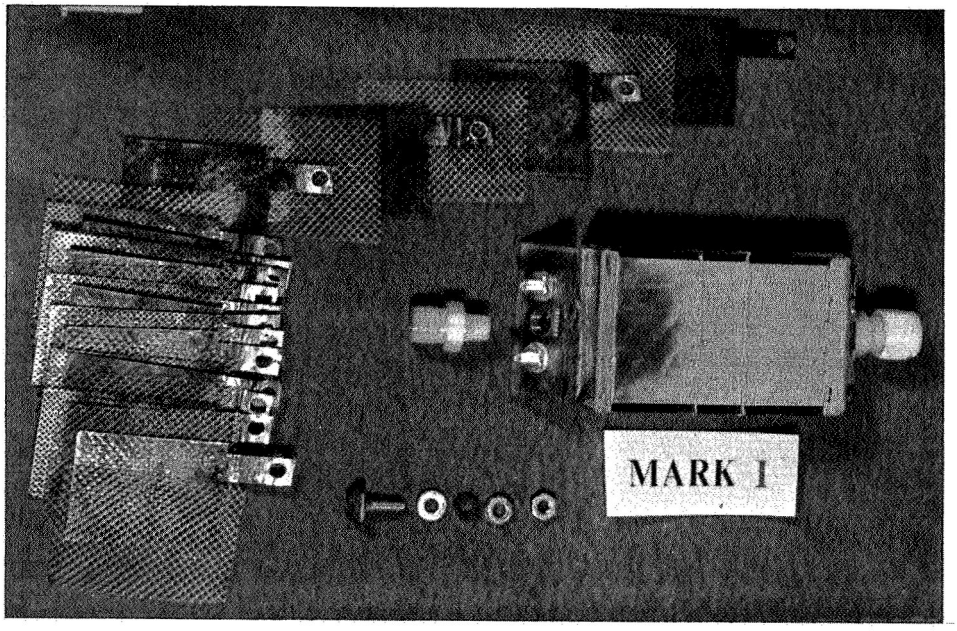

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Figure 2. Mark I Electrolysis Cell

wide, and 6 cm long. A polypropylene corrugated screen was placed between each electrode to produce and hold the desired electrode spacing. Sheet nickel or platinum leads 0.005 inch thick, 1 cm wide, and 3 cm long were spot welded to each electrode and all the leads were secured to their respective terminals, stainless steel bolts and nuts coated with a protective epoxy material.

The entire electrode assembly was packed into a small 1-inch by 2-1/4-inch by 3-3/4-inch clear polysulfone plastic box that had a sealed top cover and nylon 1/4-inch tube fittings at each end for the urine flow through the cell. The platinum electrodes were platinized after they were assembled and sealed in the plastic case to insure the best possible platinization.

The Mark I cell was used in conjunction with a continuously circulating urine flow system. This system was a sealed loop also connected to a gas volume measuring system, all of which was sealed to exclude air from the apparatus. This system is shown in Figure 3.

The urine circulating loop consisted of a peristaltic circulating pump, 1/4-inch I. D. vinyl plastic flexible tubing, nylon tubing fittings, helium purging lines, the electrolysis cell, a 500 ml dispensing burette, and a 100-ml side-tube test tube. The burette was arranged to serve as an impingement type gas-liquid separator and this reservoir prevented foam and gas from entering the pump. The 100 ml side-tube test tube was located at the low point in the loop to serve as a solids settling trap to prevent any big solids from entering the close passageways in the electrolysis cell. Initially, the gas volume measuring system consisted of a gas delivery tube leading from the gas-liquid separator section to an inverted, water-filled, graduated, gas measuring tube. The gas volume measuring tube contained a rubber septum for taking gas analysis samples. Gas leakage was encountered in the first few experiments and an improved gas collection system (described later in detail) had to be developed to eliminate very tiny leaks that affected the gas composition and volume collected over the long time periods of cell operation.

Before each experiment, the complete system was purged with helium to the point where the nitrogen measured less than 0.1 percent by volume after the urine was added to the circulating loop. A Beckman, model GC-2A, gas chromatograph with a type 13 X molecular sieve column was used to measure gas compositions. Organic nitrogen analyses were determined by the Kjeldahl method. The electric dc power to the electrolysis cell was supplied and regulated by a Sorensen, model QRC40-4A, power supply.

Mark II cell. — The results of the electrochemical oxidation experiments conducted with the MARK I cell indicated that substantial power reductions could be obtained by operating the cell to facilitate the rapid removal of gases from the liquid phase. The rapid removal of gases was facilitated by changing the urine flow geometry and operating under a reduced pressure applied to the gas phase above the urine reservoir. The MARK I cell with its urine circulation system and, especially, the gas collection and volume measuring system was not originally designed to operate under reduced pressures.

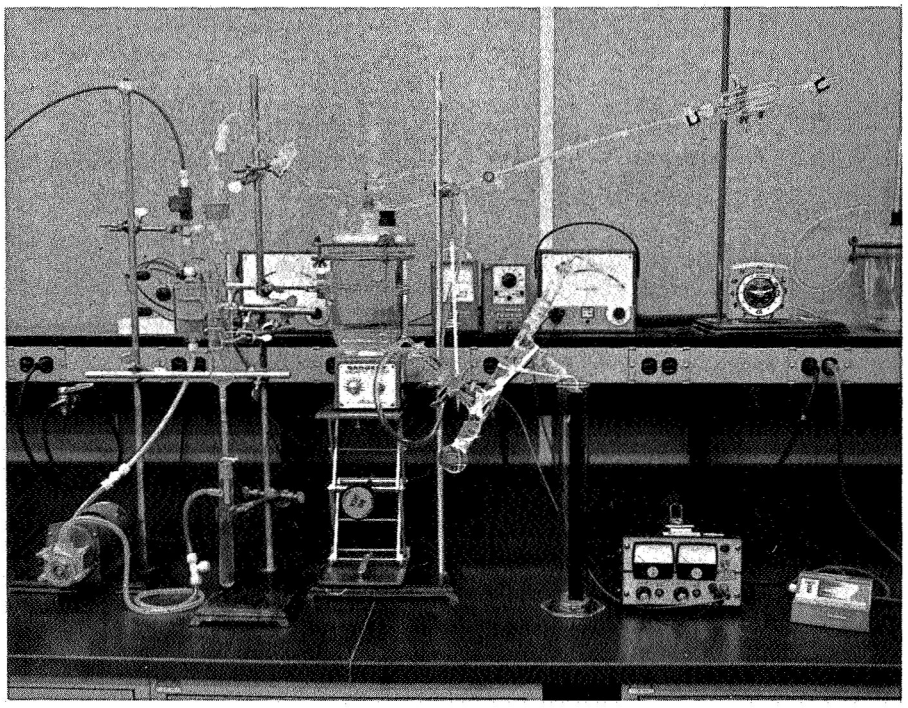

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Figure 3. Mark I Electrolysis System

A MARK II laboratory electrolysis cell with a suitable sealed urine circulation and gas collection system was designed to operate under reduced pressures. The MARK II electrolysis cell parts and housing are shown for comparison with the MARK I cell housing in Figure 4. The same platinum electrodes used in the MARK I cell were used in the MARK II cell. The epoxy coated stainless steel terminal bolts and nuts used for connecting the platinum electrode leads in the MARK I cell were replaced by platinum wire sealed through the cover of the MARK II cell and nylon bolts and nuts were used in connecting the electrode leads. This last design modification was made to preclude a faulty or poor electrical connection developing during the long duration experiments required for the complete removal of urea.

The MARK II cell was also designed to be a more versatile and improved device over the MARK I cell in several other ways: The design facilites the ease of disassembly, cleaning, internal component replacement, and assembly. Since it was a larger cell, a larger quantity of urine could be pretreated and this was necessary to withdraw urea and chloride consumption-rate analysis samples at intervals over long duration experiments. The larger size also facilitiated the ease of fabricating different internal component arrangements for evaluating the effect of different modes of cell operation. One of these modes examined using suitable internal components was the use of inert porous separators to separate the anolyte and catholyte streams in the electrode compartment and to maintain this separation to some point outside the cell after gas-liquid separation has taken place within the cell on one of these streams. Separate stream wet-chemical and gas analyses were then possible. These separators were made by cementing a loosely woven ASAHI electrodialysis-type turbulator, spacer screen on both sides of a 0.0025-inch thick nonwoven porous fabric of Dynel fibers bonded together by hot calendering. This arrangement maintains the proper plane spacing between electrodes and also separates an anolyte electrode stream from a catholyte electrode stream. The MARK II cell and one of the separators are shown in Figure 5. The components of the MARK II cell were potted in a special compound.

The special compound was a hot melt blend of 30% ULTRATHENE UE634 (Ethylene-vinyl acetate copolymer supplied by U.S.I Chemicals, Division of National Distillers & Chemical Corp.) and 70% Parowax (N.F. Paraffin wax, m.p. 126°F, supplied by the American Oil Company).

The total free volume within the MARK II cell was measured and found to be 108 ml. The ratio of cell free volume to anode area is 0.13 ml/cm^2.

Gas collection system. — The gas collection system used with the MARK I cell was only capable of collecting and measuring the volumes of nonreactive permanent gases evolving under a total pressure of one atmosphere. Since an increase in performance with operation under a reduced pressure was indicated, a more capable gas collection system had to be designed to be operated in conjunction with the MARK II cell with gases evolving at pressures less than one atmosphere. In addition, the MARK II gas collection system has the capability of collecting and measuring the amounts of any reactive (Cl_2) or vapor-type (NH_3) gases that might be evolved. These two gas collection systems, the one used with the MARK I cell and the one used with the MARK II cell, are described completely below.

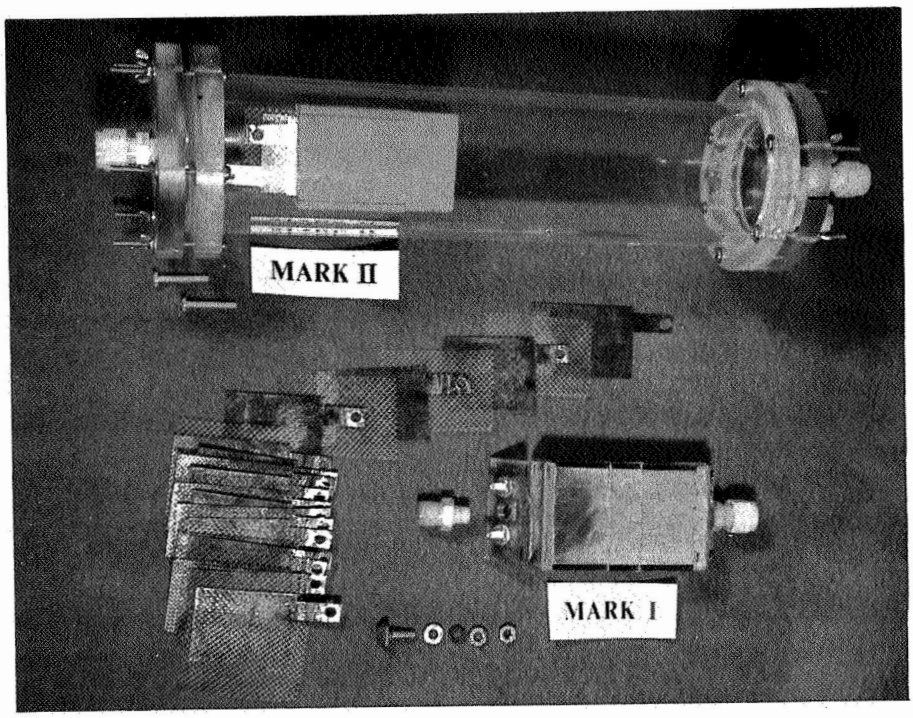

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Figure 4. Mark I and Mark II Electrolysis Cells

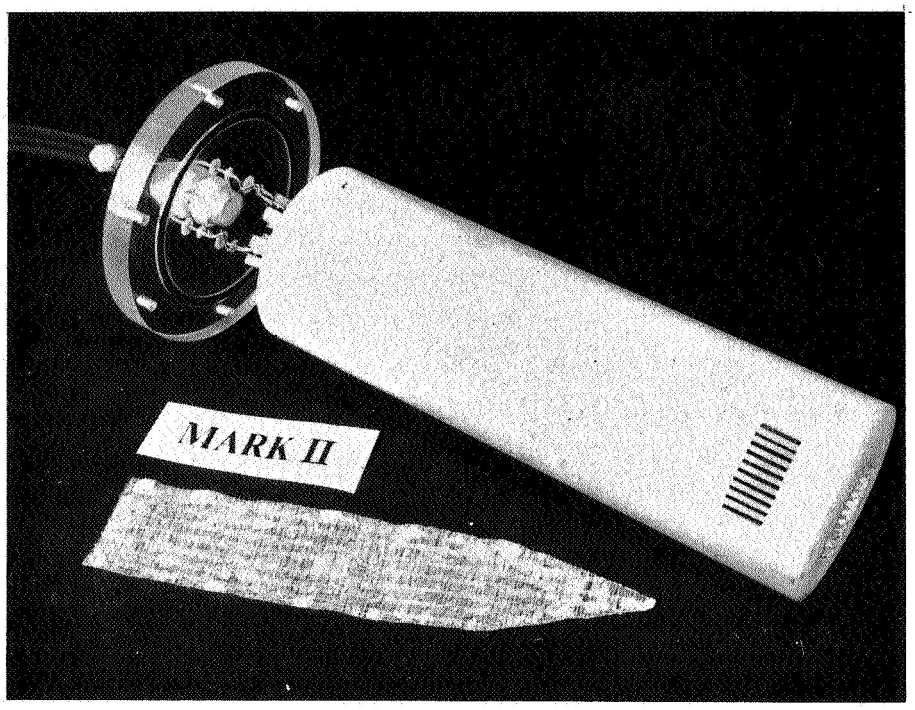

Figure 5. Mark II Cell and Special Porous Separator

Two systems were designed for the collection and volume measurements of gases evolved during the electrochemical oxidation of urine. One system is used where the gases are evolved under a total pressure of one atmosphere; the other system is required where the gases are to be evolved under a total pressure that is less than the ambient pressure. Both systems accumulate the gases at very near ambient pressure whereupon, water or some other suitable fluid at ambient temperature is displaced into a graduated cylinder so the gas volume can be measured. A gas syringe septum in the gas collector permits very small samples to be withdrawn from the sealed system for gas chromatographic analysis.

The ambient pressure gas collection system, shown in Figure 6, is used where the gases are evolved under ambient conditions which usually are a total pressure of one atmosphere and a temperature of 75°F. Referring to the details shown in Figure 6, comments covering its function and more important components and the procedure for operating this gas collection system are as follows:

The urine-gas mixture flowing out of an electrolysis cell enters into the top section of a urine-holdup reservoir. Gas and liquid are separated in this top section so that as newly created gas is evolved, gas flows over into a gas-inlet dip tube and bubbles up into the top section of a resin-reaction flask gas collector. An equal volume of water flows out of the resin flask through a water-outlet dip tube spilling out of a sealed system over a spill-over dam where its volume is measured in a graduate. For simplicity, it is assumed in this discussion that distilled water is the liquid that is used to fill the resin flask and is displaced over into the graduate; various water solutions or other liquids may be used if water reacts unfavorably with the collected gas.

Referring to Figure 6, it can be seen that since the water surface spilling over the dam at the height, h_2, is at the barometric pressure, the relationship between h_2 and h_1 and between h_2 and h_3 determines the total gas pressures sealed off in the top sections of the gas separator and gas collector, respectively. Since the height, h_2, is adjustable because it is connected by flexible tubing and the height, h_3, changes with the amount of gas collected, the height relationship between h_1, h_2 and h_3 must always be measurable in order to be able to calculate the exact quantity of gas collected.

In addition to measuring the barometric pressure, the ambient temperature and the water temperature, T, in the gas collector must be measured in order to be able to correct the gas volume for temperature, pressure, and water vapor partial volume. (Water vapor partial volume correction is about 3% at 76°F). The equilibrium condition for temperature and water vapor partial volume is ensured by the sparing use of a magnetic stirrer. (This device will add heat to a gas collector system).

The composition of the gas in the gas collector is analyzed by gas chromatography by withdrawing very small samples into a gas syringe through a septum located at the top of the gas collector. Large samples of the gas may be withdrawn by transfer to a gas sample tube. Water stored at the height, h_4, in a graduated filling-funnel addition tube flows down into a sealed gas collector to replace the gas transferred over into the gas sample tube.

All of the components of the gas collection system shown in Figure 6 are sketched so as to be easily recognized as readily available items commonly carried by any scientific laboratory apparatus supplier. The sealed gas collection system is constructed mostly with Pyrex #7740 glass and vinyl plastic flexible tubing. Three constructional details are important to the accuracy of the gas collection and volume measurement system: The complete system must be watertight and gastight over long time periods; the internal volume of any part in the entire system must not change with differential pressure changes; and the total gas volume of the gas separator section, the flexible lines through S_1, and the gas-inlet dip tube must be kept as small as possible.

The gas collector vessel is a 2-liter resin reaction flask that is leakproof when the flat ground joint is lightly greased and secured with cover clamps. A stainless steel wire suspends a short precision thermometer, T, inside the resin flask from a stainless steel hook cemented by epoxy glue to the inside of the resin flask cover. A red-rubber serum or vaccine bottle stopper (Army Medical Corps type) is used as the gas syringe septum, since this stopper fits tightly into a standard taper ground joint. These stoppers do not last too long and should be replaced regularly.

After assembling a clean empty gas collection system as shown in Figure 6 with all joints greased properly, with all stopcocks closed, with the dam height, h_2, set at 1/2 to 1 inch above the bottom of the gas-inlet dip tube, h_1, the gas syringe septum is removed and distilled water is added through this port until the water surface is about 1 to 2 inches below the resin flask cover. The gas syringe septum is replaced securely back into its port after opening stopcock, S_2. With S_2 open, a slow, fine stream of distilled water is added carefully to the addition tube from a polyethylene squeeze bottle so as to remove all of the air from the addition tube and end up with a solid column of water up to the top of the addition tube, h_4. Keeping the water level always up near h_4, the spill-over dam apparatus is removed from its holding clamp and held by hand so that when stopcock, S_4, is opened slightly, a column of water flows out the water-outlet dip tube and replaces all of the air in this line out through S_4. The dam apparatus has to be turned about 120° counter clockwise to get all of the air out of the stopcock, S_4, and the next section up through the 75° elbow. (Suction may also have to be applied to remove all the air from this line.) When the water level is up to the spill-over point, this apparatus is placed back in its clamp, S_4 and S_2 are closed and stopcock, S_5 is opened. The gas collection system is now almost exactly in the same condition as it would be when a gas collecting experiment has been conducted and a new experiment is about to be started.

The new gas evolving experiment is set up with S_4 closed and with S_1 open to the gas separator and with S_3 open to overboard, helium gas is admitted through needle valve, V_1, to purge all of the air out of the gas separator section and the gas-inlet dip tube. Water is admitted to the resin flask via S_2 until the gas volume in the resin flask is only large enough to still allow adequate purging of the top section of the flask. Purging is continued until a gas sample obtained through the gas syringe septum reveals the required level of air contamination desired. Helium flow is stopped by closing V_1 and S_1, and the resin flask filled completely with water via S_2 up through

S_3 open to overboard. S_3 is closed and the gas-inlet dip tube completely filled with water via S_2 up through S_1 open to overboard. S_1 is closed and the gas syringe septum section completely filled with water via S_2 by inserting a very fine hypodermic needle just through the septum membrane so as to allow the inflowing water to force gas out the needle. When water flows out the needle, it is removed. The resin flask gas collector vessel should now be completely filled with water and the water level at h_2 should be just ready to spill over the dam. (Water is added via S_2 by opening S_4 until it spills over dam then S_2 is closed.) With all stopcocks closed except S_4 and S_5, the gas collection system is now in a condition to see if it has any leaks. A gas leak will allow water to spill slowly over the dam.

When about ready to start collecting gas, with only S_4 and S_5 open, S_1 is opened to the gas separator. The water level at S_1 will fall down into the dip tube and water will spill over the dam. This water is discarded and the level of the water in the gas-inlet dip tube is marked with ink or tape. This is the usual water-starting level for the electrochemical oxidation of urine experiments and at this level, the total pressure in the gas separator section is less than the barometric pressure at the start by the difference between this level and h_2 in inches of water pressure. The key point here is that the total gas pressure in the gas separator section must be brought back to this same exact pressure at the conclusion of the gas collecting experiment in order to determine the total volume of gas evolved. The gas collecting experiment is conducted and the water spill over is collected in a suitable graduate. If the experiment requires a long period, the open end of the graduate is sealed with plastic food-wrapping film to prevent loss of water by evaporation.

At the conclusion of the gas collecting experiment and after the gas and water temperatures have been stabilized to the starting temperature, S_4 is closed and the graduate with the collected water (its water level reading is noted) is replaced by a second, smaller, empty graduate. In essence, what has to be done at this point is to carefully add small quantities of water to the resin flask via S_2 keeping track of the exact quantity added from the graduated funnel until the total pressure in the gas-inlet dip tube is slightly higher than the barometric pressure so some of the excess gas in the dip tube can be bled overboard via S_1. This operation can only be accomplished successfully by careful manipulation toward the final exact condition that puts the system exactly at the marked water-starting level when S_2 is closed, S_1 is open to the gas separator section, and S_4 is open to the spillover dam. It is difficult to remove the exact amount of excess gas overboard via S_1 from the gas-inlet dip tube section. When this is accomplished and S_4 is finally left open with water up to the spillover dam height, h_2, the total volume of water added from the graduated funnel via S_2 minus the total volume of water spilled over into the second smaller graduate is added to the total water collected in the first graduate. This final grand total volume of water is the total volume of gases evolved from the experiment (plus the water vapor partial volume) at a temperature, T, and at a pressure less than the barometric reading by the difference between h_3 and h_2 in inches of water pressure. The exact volume of gases is thus calculated and corrected to standard temperature-pressure conditions whereby the quantities collected of the different species of gas can be calculated from the gas chromatographic analysis.

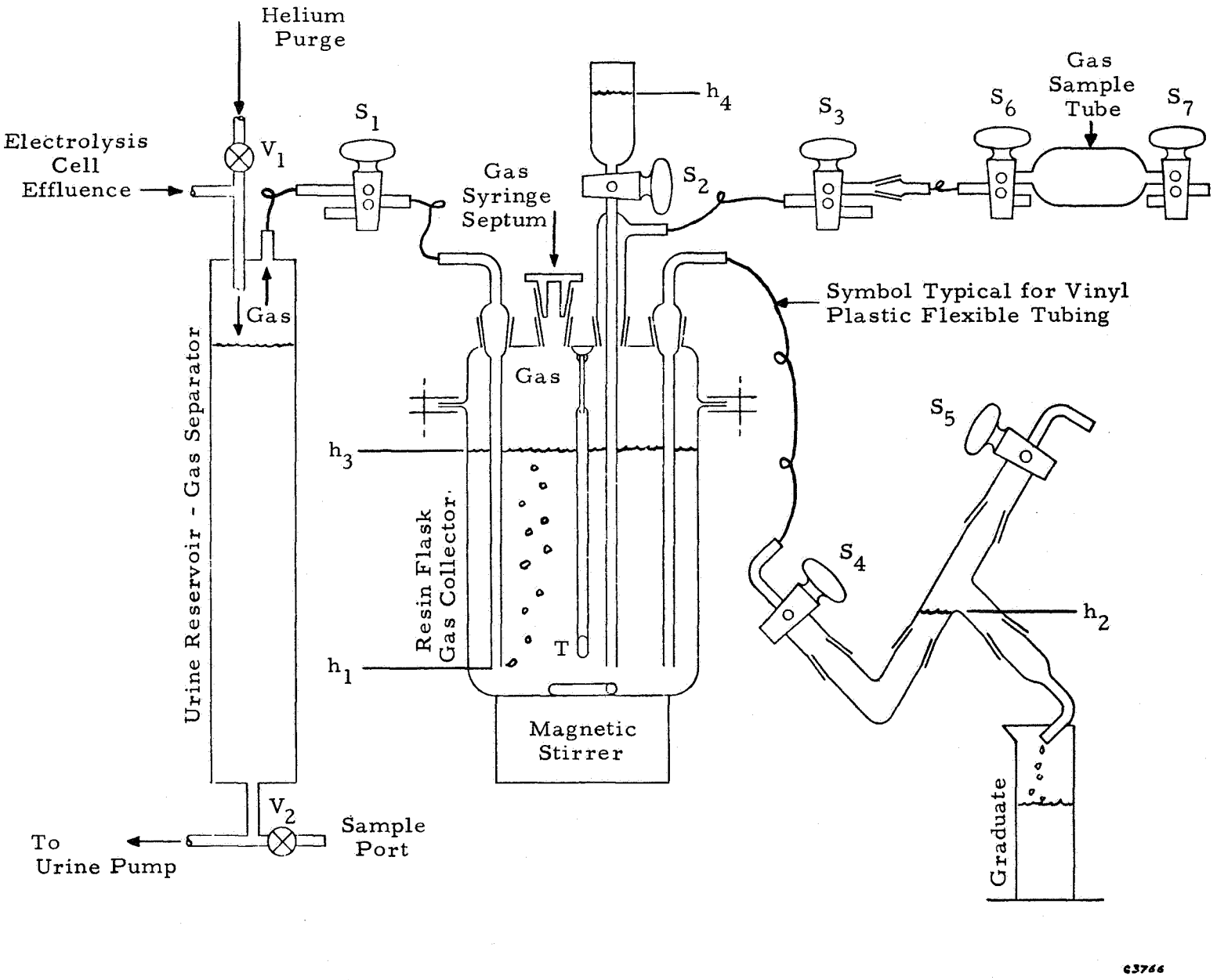

Figure 6. System for Collection of Gases Evolved at Ambient Pressures and for Volume Measurement at Ambient Pressures and Temperatures

A reduced pressure gas collection system, shown in Figure 7, is used where the gases are evolved under a total pressure that is less than one atmosphere and at ambient temperatures. Referring to the details shown in Figure 7, it can be seen that, except for some additions, this system is almost the same as the system shown in Figure 6.

The urine-gas mixture flowing out of an electrolysis cell centers into the top section of a urine-holdup reservoir, not shown in Figure 7. Gas and liquid are separated in this top section under a total pressure that is less than one atmosphere and is produced by the booster pump shown in Figure 7. This pump boosts the pressure of the gases up to a point where, as newly formed gas is evolved, gas flows over into the resin flask gas collector. This system accumulates the gases at very near ambient pressure. In addition, this system includes a gas scrubber-gas separator section. This section is required to remove and retain any gas vapors from the permanent gases through scrubbing and condensation, solution, or reaction. When small amounts of vapors or reactive gases are evolved along with the permanent gases from the urine into the low pressure region of the urine gas separator, they will be swept over into the suction line of the booster pump where they are injected into the aqueous solution that is being continuously recirculated by the pump. The peristaltic pump boosts the liquid-gas mixture pressure to the ambient pressure in the gas scrubber-gas separator section. The recirculating aqueous solution is designed to retain the vapors and reactive gases and allow the permanent gases to flow over into the gas collector. Small amounts of gases such as chlorine, ammonia, and carbon dioxide may be trapped and their presence detected and measured. A mercury manometer is used to measure the reduced pressure in the urine gas separator section.

The booster pump must have the capability of producing a low suction pressure while pumping a liquid-gas mixture and still handle the total volume of gases evolved. The pump must be able to operate continuously (although in actual use, it is not), have a wide range of chemical resistance to various aqueous solutions, and not add any contamination to the solutions being pumped. The best booster pump found so far is the #7021-15 MASTERFLEX TUBING PUMP, using U. S. Stoneware, Inc., #R-3603 TYGON TUBING (3/16" ID x 3/8" OD x 3/32" wall). This peristaltic pump is sold by Cole-Parmer Instrument and Equipment Co., 7330 North Clark Street, Chicago, Illinois. At least three feet of TYGON tubing is used with the pump and this is assembled at the start so that a minimum length of tubing is protruding from the pumps discharge side. Then, as the tubing becomes fatigued and is pulled through the pump head (in the direction of fluid flow) to a new fresh section, the weakened section of tubing is not on the pump suction side where it would collapse under vacuum.

Valves V_3, V_4 and V_5 are small needle valves constructed entirely of polyvinyl chloride for corrosion resistance and noncontamination. Valve, V_5, is used to choke the pump just enough to create the desired inlet suction pressure for the evolved gas flow through valve, V_4, while still allowing ample liquid flow through the pump to wash the gases. Valve, V_4, is used to shut off the evolved gas section from the gas scrubber section and to regulate the speed of the gas flow into the booster pump. Valve, V_3, is a helium purging bypass valve used to allow helium purging of the complete system.

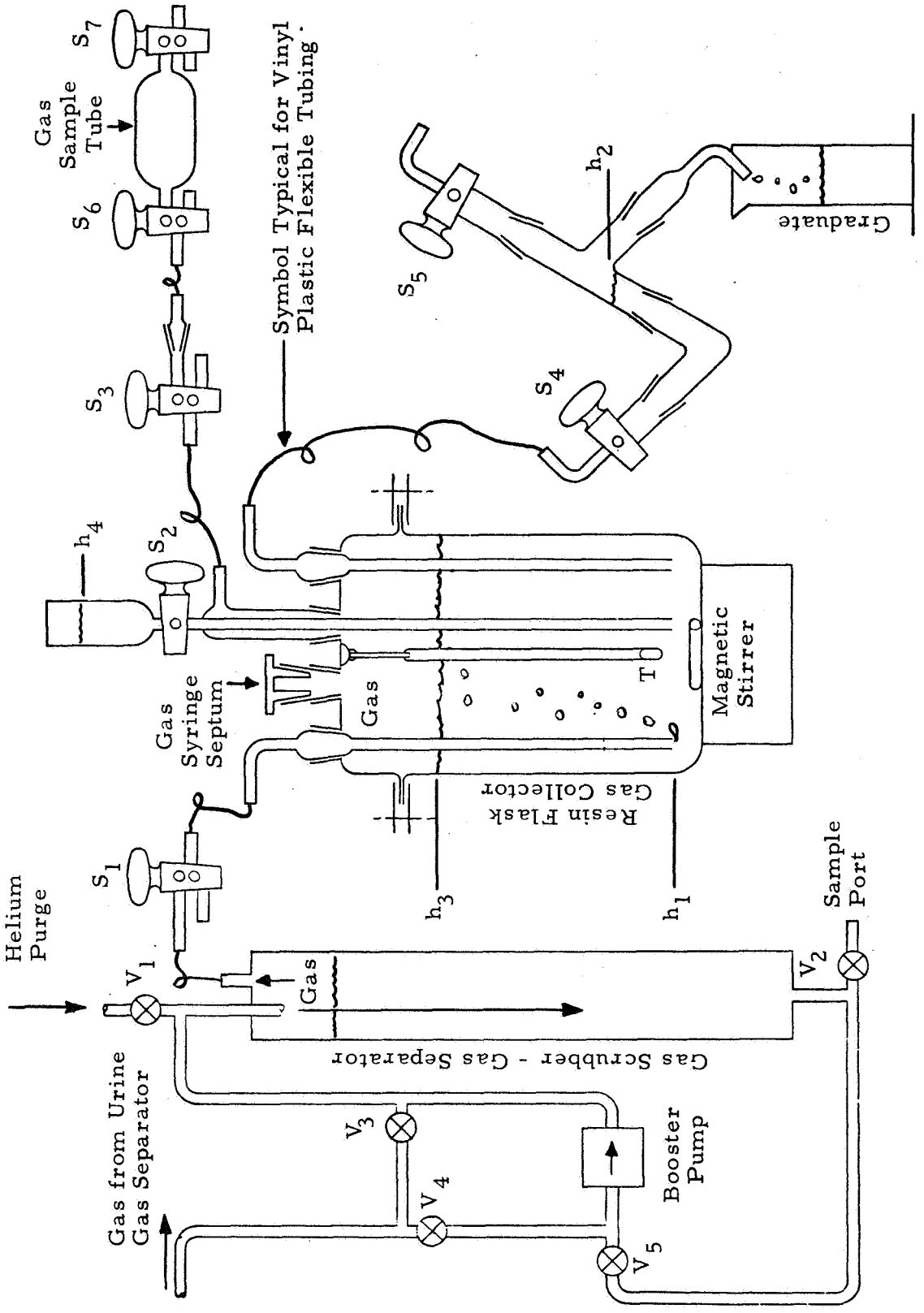

Figure 7. System for Collection of Gases Evolved at Less than Ambient Pressures and for Volume Measurement at Ambient Pressures and Temperatures

The gas scrubber-gas separator section is filled with an accurately measured quantity of the desired aqueous scrubbing solution with V_3 and V_4 closed. The scrubbing solution is recirculated briefly using the booster pump with V_5 full open and V_1, V_2, V_3 and V_4 closed, in order to separate any air trapped in this section. When this is completed and the stage is reached where the complete system is purged with gas, the helium purging will be conducted as explained in the procedure for the ambient pressure system above, except that helium will be introduced back in the urine gas separator section and not through V_1, V_5 will be closed, and V_4 and V_3 will be open. When the helium purging is completed and before the resin flask is filled completely with water, the booster pump is used to evacuate the urine gas separator section to the desired reduced pressure level and the pump is trimmed for continuous operation. This is done by closing the helium inlet purging valve and V_3 and V_4, and starting the booster pump after opening V_5. When the pump is gas-free and pumping smoothly, V_5 is closed enough to reveal moderate choking of the fluid flow through the pump. This is revealed by any liquid in the line leading to V_4 being sucked into the pump inlet and by cavitation in the liquid streaming out of V_5. When there is suction, V_4 is opened cautiously and very slowly and evacuation of the urine gas separator section is begun. Long before the desired reduced pressure level is reached, valves, V_4 and V_5, are trimmed so that their combined settings stabilize the pressure level at a higher level than that desired. At this point, V_4 is used as the fine control to reduce the pressure and stabilize it at the desired level. The urine circulating system is started and both systems are run together until there are no evolved gases being pumped over. The urine gas separator section can now be checked for air inleakage by closing V_4 and observing the mercury manometer. Valve, V_4, is trimmed back to where it was if the system is airtight.

The resin flask is filled completely with water, quickly, and the gas collecting experiment is conducted as described above. As soon as the gas collecting experiment is started and at various times during the experiment (especially during the initial period), the trim setting on V_4 (and perhaps V_5) will have to be altered to maintain the desired pressure level. The gas collecting experiment is conducted and the water spill over is collected in a suitable graduate as previously explained.

At the conclusion of the gas collecting experiment, V_4 is closed and V_5 is fully opened, and the booster pump is left running for a few minutes to stabilize the gas scrubber section. At this point, the pump is turned off and V_5 is closed. The exact quantity of the aqueous scrubbing solution in the gas scrubber section is measured and the solution is analyzed for the quantities of vapors and reactive gases retained and removed from the permanent gases.

The gas collection system together with the Mark II cell is shown in Figure 8.

Mark III cell. – The Mark III cell was designed to electrochemically treat 9 pounds of urine per day. It consisted of 16 anode and 16 cathode compartments in which the electrochemical reaction occurs. These compartments were formed by placing a separator (paper sheet), with a spacer screen on

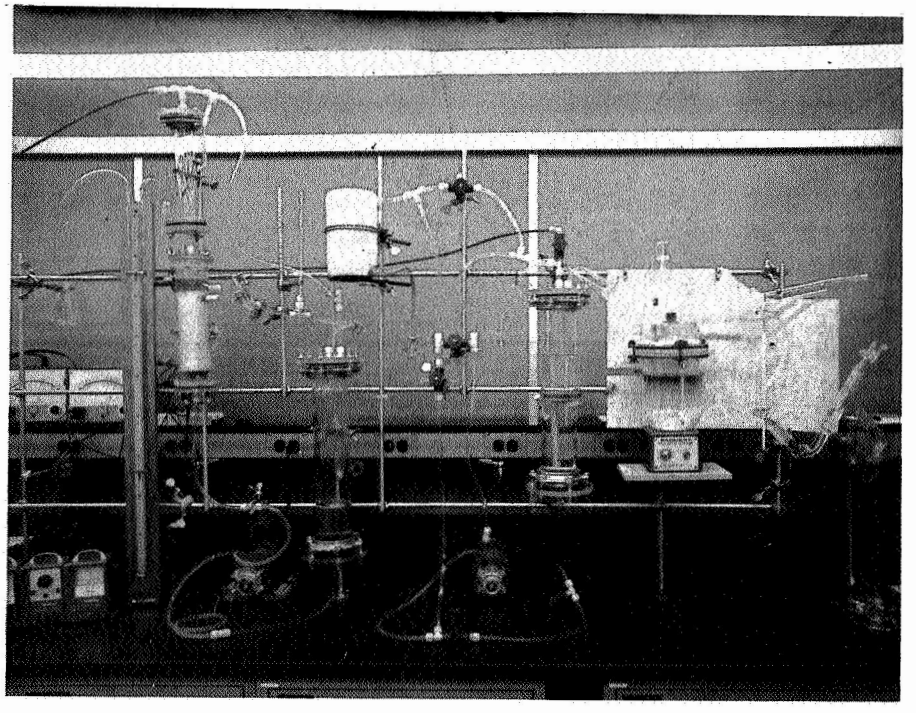

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Figure 8. Mark II Electrolysis System

each side, between the anode and cathode plates. These plates with their accompanying separators and spacers were laid alternately, one on top of the other until the entire stack was completed. Manifolding to inject new urine into each compartment and remove treated urine was accomplished in the peripheral gasket seals. One inlet and one exit port were provided in opposite corners of each compartment. Clear plastic end plates were used to allow visual observation of liquid flow across the electrode plates. This construction is illustrated in Figure 9, which shows a cross section of the pretreatment cell. Cell dimensions and materials of construction are summarized in Table I. Total useful surface area was 28,715 cm^2 for the platinum anode and 33,600 cm^2 for the stainless steel cathode. Construction details of the components of the Mark III cell are shown in Figures 10 through 14.

Figure 15 is a photograph of the Mark III cell and auxiliary system. The auxiliary system consists of two peristaltic circulating pumps, two gas-separating urine reservoirs, and a gas scrubbing column (not shown). One pump and reservoir handle the anolyte and the other combination handles the catholyte. Each pump is rated at 1400 ml/min and the liquid flow pressure drop through the cell was found to be influentually small. Each urine reservoir contains the impingement type gas-liquid separator employed successfully so far in this program. All of the tests conducted with the MARK III cell have employed the figure-8 electrolyte flow circuit. This is where the urine in the anolyte urine reservoir is next pumped through the catholyte section in the electrolysis cell and vice versa. This arrangement was employed to evaluate the effect of chemical depolarization on the speed and efficiency of electrolytic pretreatment.

The total free volume within the MARK III cell was measured and found to be 2500 ml. The ratio of cell free volume to anode area is 0.087 ml/cm^2.

The cell and its associated components have merely been rinsed out thoroughly between runs with deionized water after a short soak in deionized water containing a small amount of detergent. The final five-day test in which five successive batches of raw urine were processed was conducted without rinsing between batches.

The electrodialysis stack was purchased from Ionics, Inc. Figure 16 is a schematic drawing of the stack configuration. In this configuration the electrode compartments represent a single diluting compartment. There are a total of 10 diluting and 10 concentrating compartments, all fluid flow being internally manifolded.

The length and width dimensions of the stack components are a nominal 5" x 9". Anion-transfer membranes are Nepton AR110-DYG and cation-transfer membranes are Nepton CR61-DYG both of which are manufactured by Ionics. Membrane thickness is 24 mils. The spacers are the Ionics' tortuous path spacer made from low density polyethylene having a total thickness of 40 mils. The effective cross-sectional area of a spacer is about 56 cm^2.

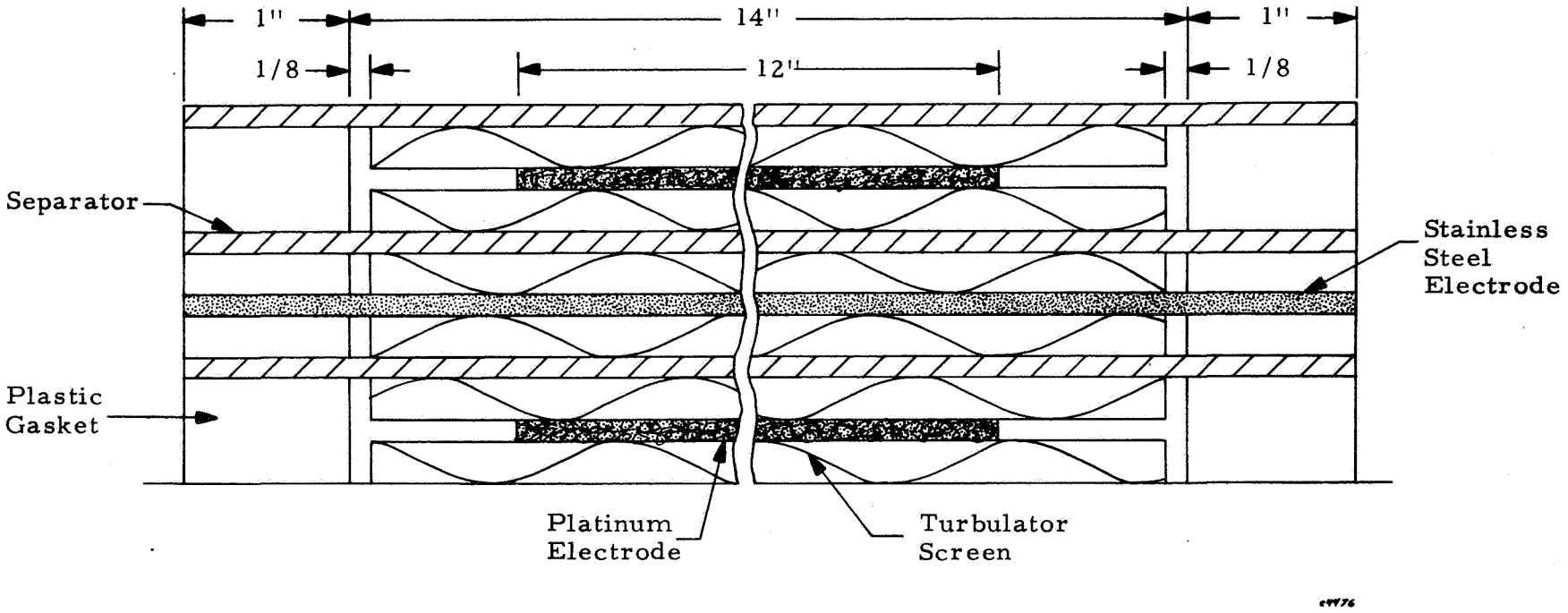


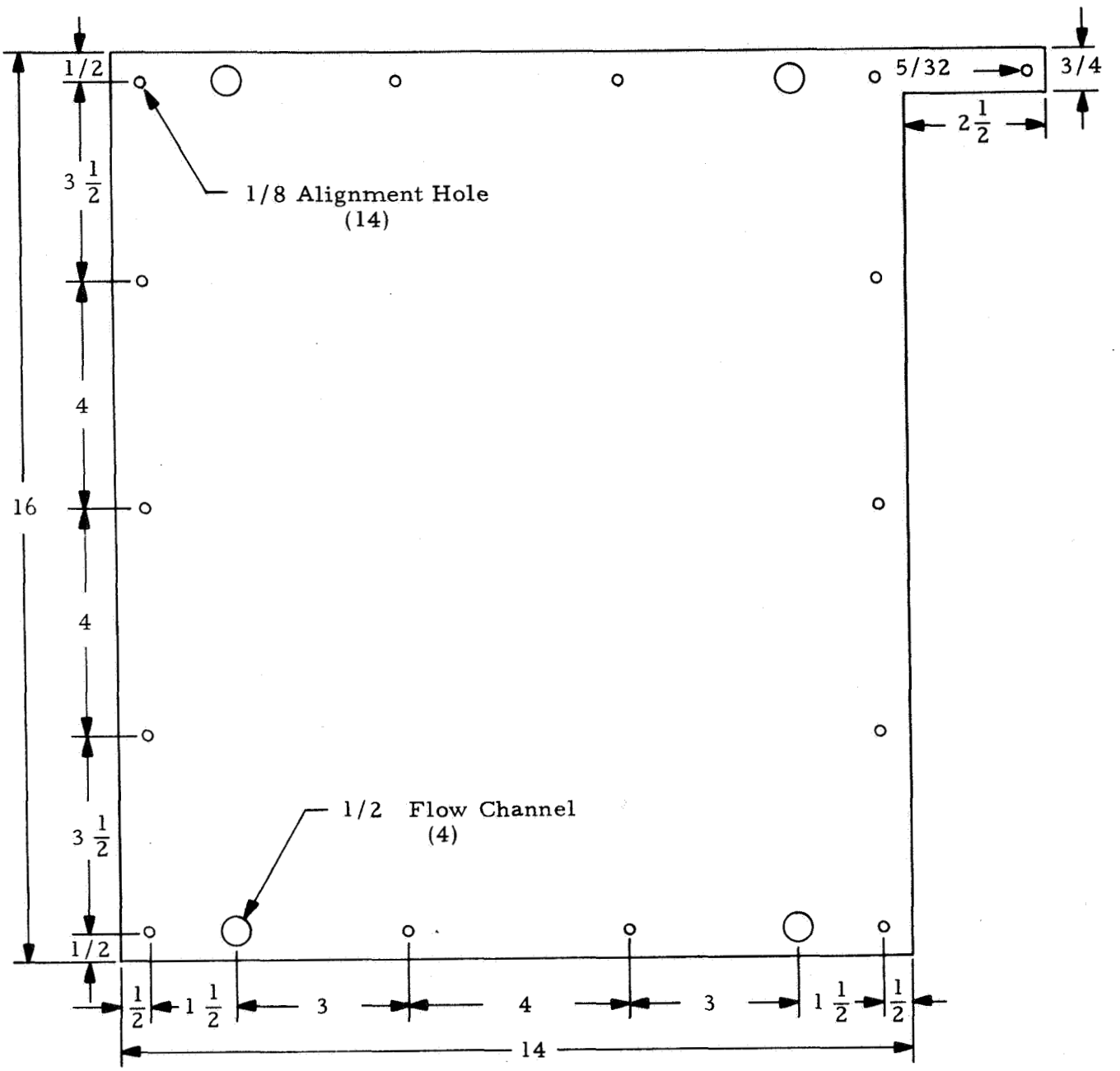
Figure 9. Cross Section of Mark III Urine Pretreatment Cell

TABLE I

MARK III URINE PRETREATMENT CELL

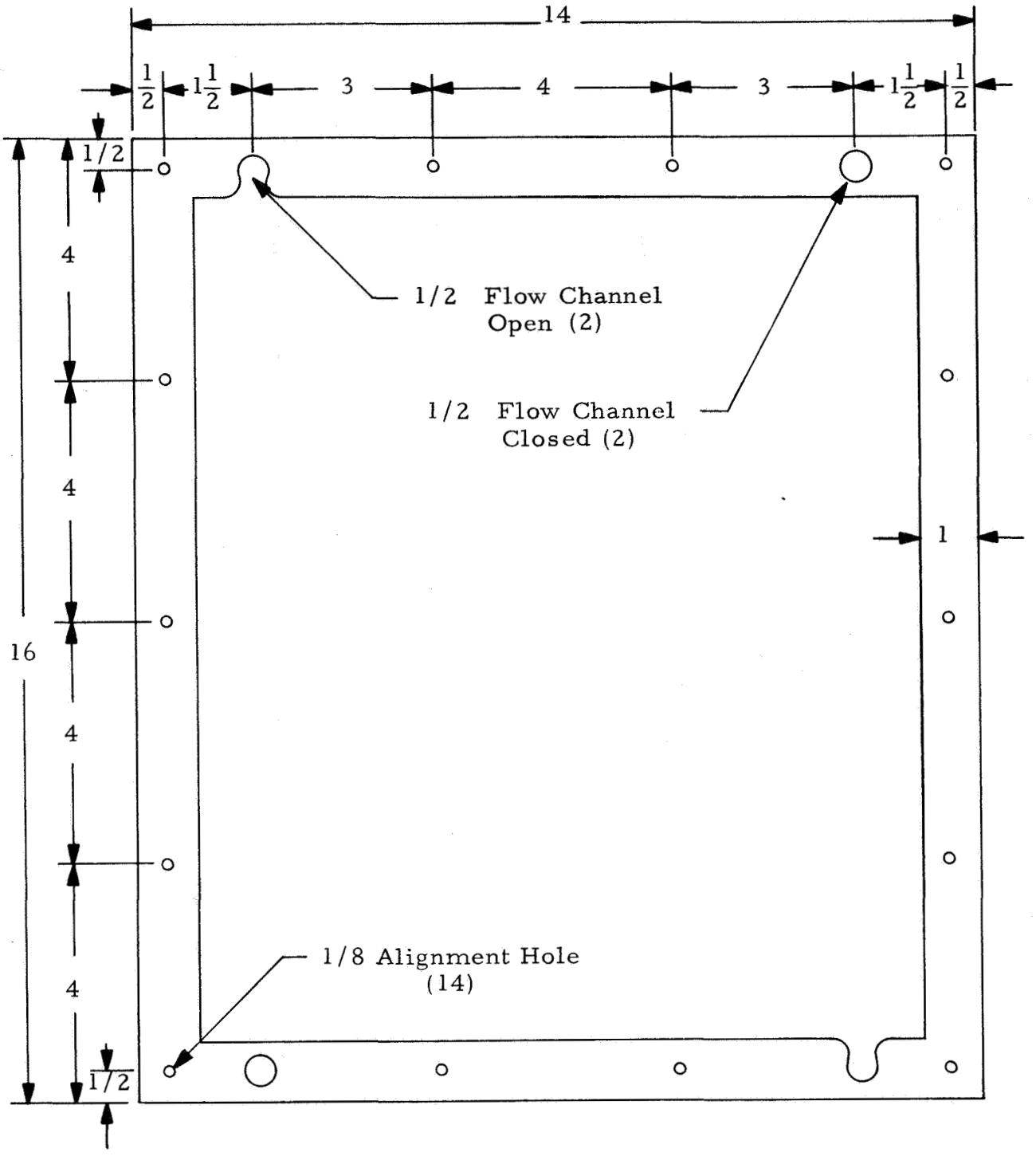
	Anode	Cathode
Electrode	Platinum	347 Stainless Steel
Thickness	0.003 in.	0.020 in.
Dimensions	12" x 12"	14" x 16"
Useful Surface Area	144 in^2	169 in^2
Number Used	16	16

Turbulator	
Material	Polypropylene Screen
Dimensions	12" x 16" x 0.020", 4 x 4 strands/inch
Number Required	64
Separator	
Material	Nonwoven Dynel
Dimensions	12" x 16" x 0.0025"
Number Required	32
Resistivity in 0.1 M KCl	1260 ohm-cm
Gasket	
Material	Polyvinyl Chloride
Dimensions	14" x 16" outside x 0.020" thick x 12" x 14" inside
Number Required	48



Material: 0.020 Stainless Steel #347

Figure 10. Nine lb/day Urine Pretreatment Cell Stainless Steel Cathode



Material: 0.010 PVC Sheet
0.024 PVC Sheet

Figure 11. Nine lb/day Urine Pretreatment Cell Gasket

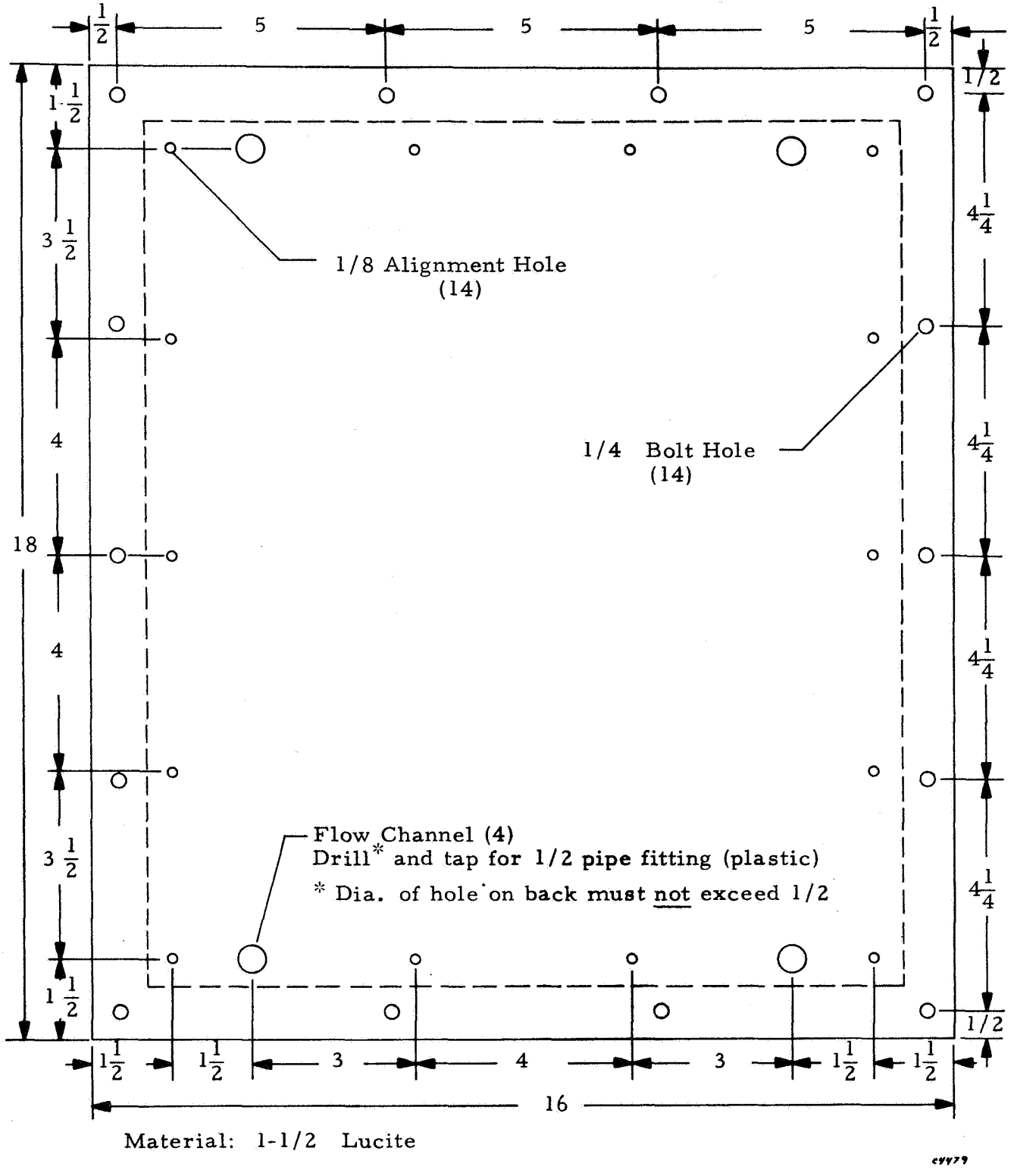
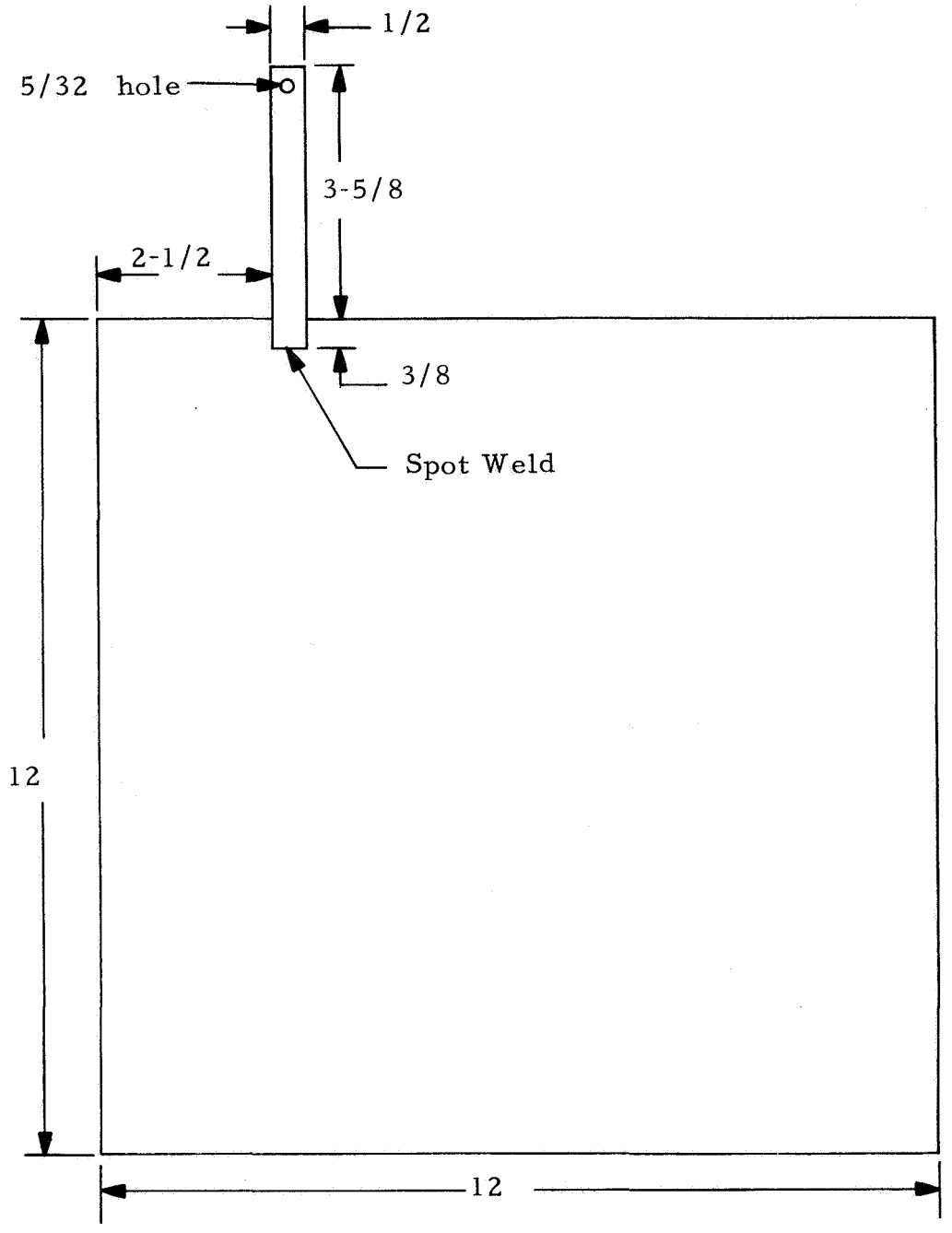


Figure 12. Nine lb/day Urine Pretreatment Cell End Plate



Material: Platinum

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Figure 13. Nine lb/day Urine Pretreatment Cell Platinum Anode

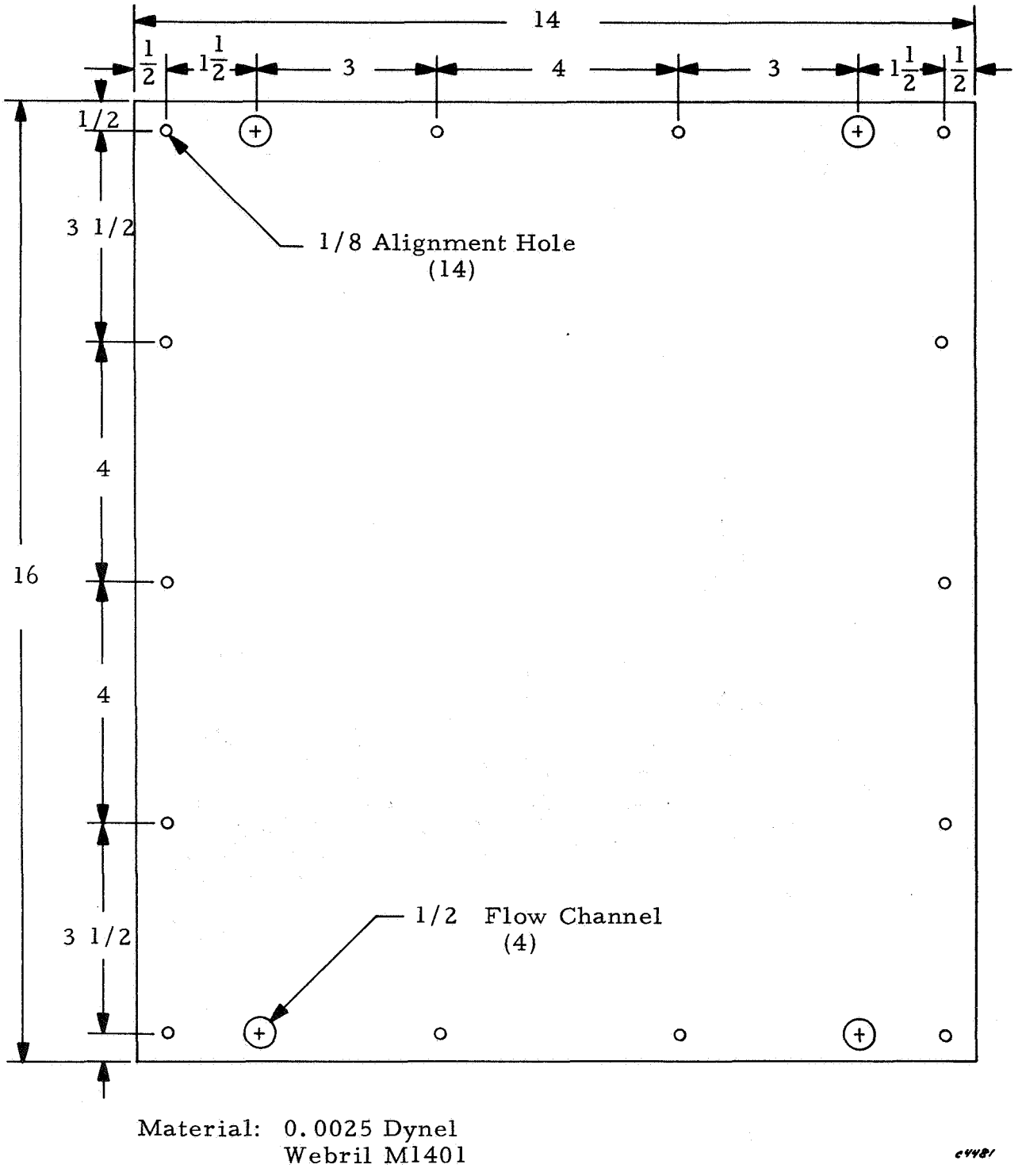

Figure 14. Nine lb/day Urine Pretreatment Cell Separator

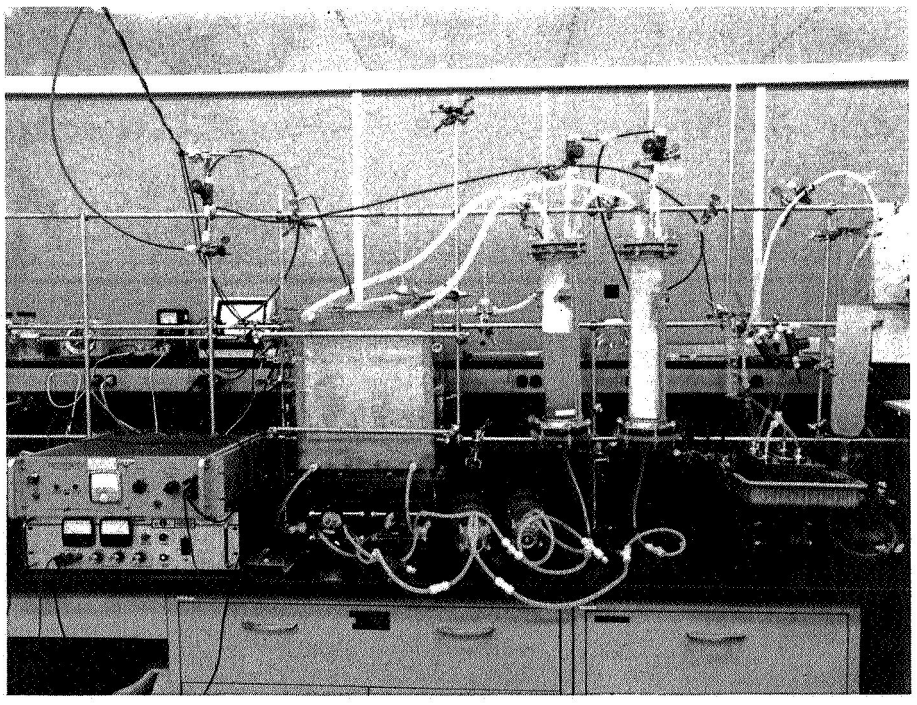

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Figure 15. Mark III Electrolytic Pretreatment Cell and Electrodialysis Stack Combined System

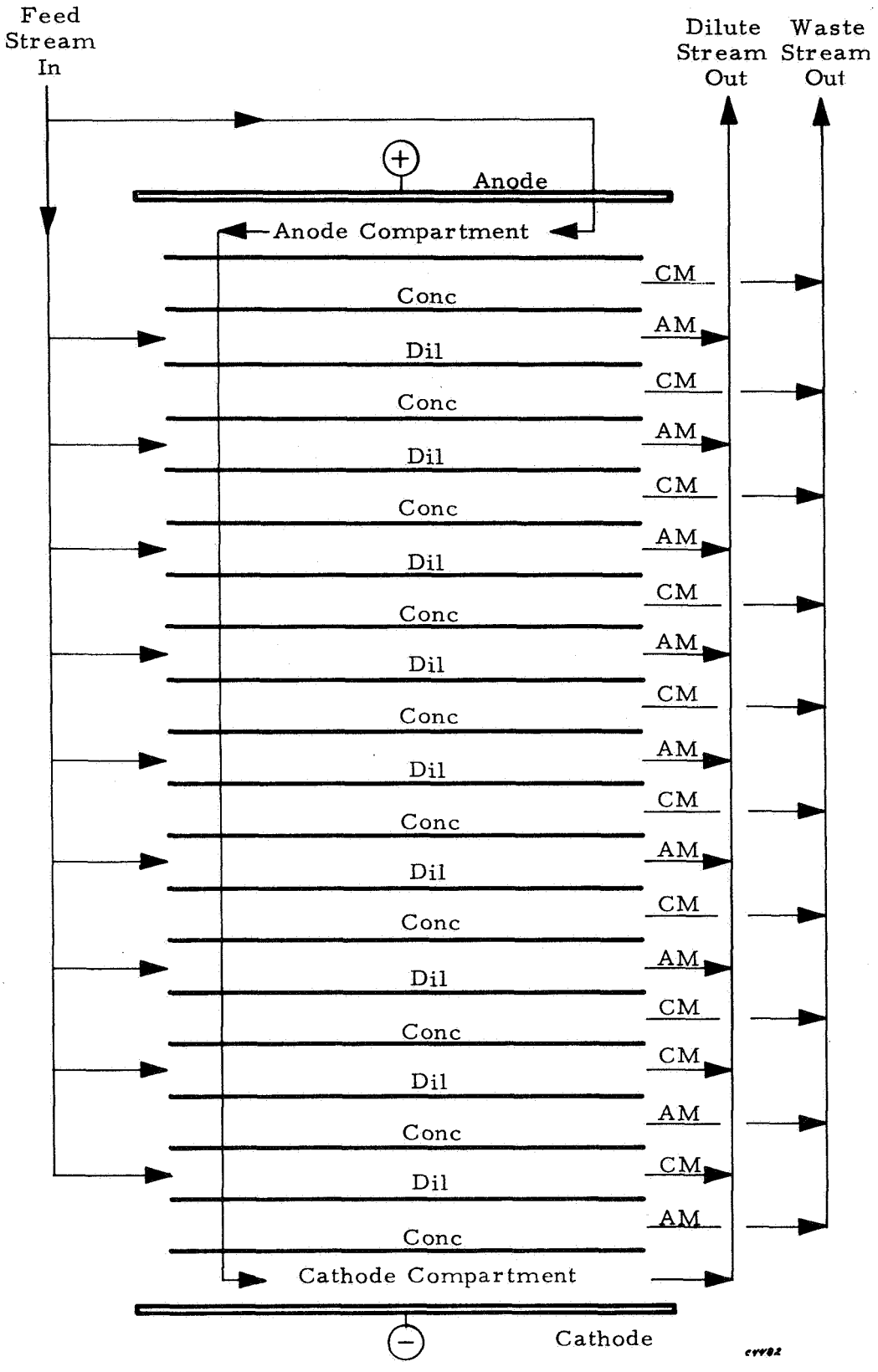

Figure 16. Electrodialysis Stack Configuration

The electrodes are at either end of the stack, the anode on top and cathode on the bottom. Each contains a tab for connection to the dc power supply. The anode is fabricated by Ionics and carries the trade name of Tirrelloy. It is a 12-mil sheet of titanium coated on the stack side with 70 microinches of platinum. The cathode consists of a 25 mil sheet of 316 stainless steel.

The entire stack is sandwiched between two 316 stainless steel pressure plates. Polyvinylchloride (PVC) blocks at both ends of the stack act as supporting structures and pressure distributors while thin butyl rubber gaskets form a seal between the PVC end blocks and the electrodes. Operated at 28 V dc and on the salt concentration of normal urine (15,000 - 20,000 ppm), the initial current is between 2.5 and 3 amps. This decreases as salt is removed to a final value of about 0.15 amps. For each liter of feed about 30 minutes of demineralization is required.

General Procedures

Analytical Procedures. — Urine pretreatment was monitored by wet chemical analysis throughout this program for Total Kjeldahl Nitrogen, urea concentration, and chloride content. The Total Kjeldahl Nitrogen (see ref. 5) includes all organic aminoid nitrogen in the trivalent state plus ammonia nitrogen. The Kjeldahl analysis does not include nitrate and nitrite group nitrogens. The urea concentration was measured by reaction with alkaline sodium hypobromite solution (see ref. 6) using a Doremus-Hinds Ureometer. Although this method is not as accurate and appears to give lower values than the Kjeldahl method, it is rapidly performed and was used to monitor the removal of urea during the 5-day demonstration test with the MARK III cell. Chloride analyses were determined by the Volhard-Arnold method which would include all halides as chloride (see ref. 6).

Urine pH was measured with a Beckman Zeromatic pH meter. Urine specific conductivities were measured with an Industrial Instruments Inc., Model RC-16B2 Conductivity Bridge using a platinum cell with a constant of 10 cm^{-1}.

A Beckman, Model GC-2A, gas chromatograph with a type 13X molecular sieve column was used to analyze gas compositions. The 13X molecular sieve column will separate hydrogen, oxygen, nitrogen, methane and carbon monoxide. Neither carbon monoxide nor methane were ever detected from urine electrochemical pretreatment experiments.

Data Recording and Reduction. — The electric dc power to the electrolysis cells was supplied and regulated by Sorensen Models QRC40-4A, QRC40-30A and DCR40-20A power supplies. The electrolysis cell voltage and current were metered by Weston Model 911 meters. Voltages were recorded by a Bausch & Lomb, (10mv) VOM5 recorder. Currents were recorded by using Westinghouse ±1/4% accurate shunts with a Leeds & Northrup Co., (10mv) Speedomax G recorder.

Simple data reduction was performed with a Friden 132 Electronic Desk Calculator. An Olivetti-Underwood Programma 101 was programmed to calculate all dc watt-hour and dc amp-hour values using the Prismoidal Formula and entering appropriate short or long time interval values of voltage and current taken from the recorded charts.

Results and Discussion

Catalyst Screening. – The results of the evaluation test for the candidate catalysts are shown in Table II. This table shows the percentage of gas evolved at three and five minutes from the start of the reaction for each catalyst evaluated and the amount of each catalyst added in grams per pound of urine. The reaction in a few of these tests was too vigorous to measure the rate of gas formation.

The results shown in Table II indicate that most of the candidate catalysts are significantly effective in increasing the rate of the reaction when as little as 0.05 grams are added to a pound of urine. These results indicate that the most promising catalysts are the Astropower catalyst 7765, ultra-violet light with mercury, ferric chloride, cerous chloride and cupric chloride. Catalyst 7765 is equivalent to Haloset 4-1.

The oxidation reaction was too violent for gas measurements at catalyst additions of 5 grams and 0.5 grams per pound of urine. It was found necessary to use only 0.05 grams per pound of urine and also to add 30 to 60 ppm Dow Corning Antifoam C to the urine to prevent foam from being carried into the gas measuring system. The results indicate that the Antifoam C had a retarding effect on the rate of the reaction. The catalytic power should therefore be compared only with the no-catalyst test data given in line 4 of Table II where the effect of Antifoam C is shown.

The rate of the oxidation reaction was too vigorous for gas measurement even at 0.05 grams of ferric chloride per pound of urine. An additional test was performed where deionized water was substituted for the urine. The object was to determine if the ferric chloride catalyst was decomposing the hypochlorite without oxidation of the urine organics. There was no gas evolution and no apparent decomposition since the loss of hypochlorite measured by iodine titration was only 2.1% after 17.5 hours.

In all tests analysis showed that 88 to 97% of the organic-nitrogen of the urine was oxidized by the hypochlorite. These organic nitrogen analyses gave results as Total Kjeldahl Nitrogen. The incompleteness of the oxidation was due to the variance of natural urine in organic nitrogen content when a constant amount of hypochlorite was added in each test. The composition of the evolved gas during each reaction was periodically analyzed, and the amount of N_2 ranged from 87 to 93% by volume. The remainder was helium and O_2 where the O_2 varied from 1 to 2% by volume in most cases, and 3 to 5% in only two cases.

Mark I Cell Experiments. – The results of the Mark I operational performance experiments are shown in Tables III, IV and V. These tables show the urine modification at the start of each experiment, the constant voltage imposed on the cell and the cell performance values obtained. Summaries of the Mark I experimental conditions and experimental results are shown in Tables VI and VII.

TABLE II

CATALYST EFFECT ON HYPOCHLORITE OXIDATION OF ORGANICS IN URINE

Catalyst	Amount Catalyst Gram/Pound Urine	Amount Dow Corning Antifoam C PPM	Percent Gas Evolved At Three Minutes	Percent Gas Evolved At Five Minutes
None	0.00	0	91.2	98.5
7765(4)	5.00	0	(1)	
7765(4)	0.50	0	(1)	
None	0.00	30	82.8	85.9
7765(4)	0.05	30	94.0	98.8
$CeCl_3$	0.05	30	95.0	99.3
$CuCl_2$	0.05	30	96.0	99.0
$FeCl_3$	0.05	30	(1)	
$FeCl_3$	0.05	60	(1)	
$CrCl_3$	0.05	60	91.0	93.5
9201(5)	0.05	60	86.8	91.1
$NiCl_2$	0.05	60	86.2	89.5
$MnCl_2$	0.05	60	83.4	88.4
$FeCl_3$	0.05	60	0.0(2)	0.0
UV+Hg	0.0171	60	(3)	100.0

(1) Reaction too vigorous for controlled gas measurements.
(2) Deionized water substituted for urine.
(3) Hypochlorite added slowly over 5 minute period.
(4) Astropower Laboratory catalyst 7765 (Haloset 4-1).
(5) Astropower Laboratory catalyst 9201.

TABLE III

MARK I ELECTROLYTIC PRETREATMENT CELL PERFORMANCE SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Overall Time Average Cell Voltage volts	Period Overall Time Average Cell Current amps	Period Overall Time Average Anode Current Density mA/cm^2	Period Watt-Hour Input per Pound of Water(2) wh/lb	Period Faradays Required per Mole of TKN(1) F/n	Period Overall Time Average Watt-Hour Input per Pound of Water(2) Required to Remove 1.0 g TKN(1)/ℓ wh/lb g/ℓ
7060701 11.2 Hours	None 6.34 - 5.68	Constant 1.90	0.234	0.732	4.48	4.15	6.79
7060802 11.2 Hours	Added #7765 Catalyst at 1.21 g/lb. 5.68 - 4.60	Constant 1.90	0.282	0.881	6.04	3.39	5.59
70601202 12.5 Hours	Added $FeCl_3$ Catalyst at 0.068 g/lb. 4.60 - 3.27	Constant 1.90	0.232	0.725	6.25	2.84	4.70

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.

(2) This value is based on the actual volume of the urine being processed, where it is assumed that each liter of urine at any stage in the electrolytic pretreatment process contains 2.20 pounds of water at 75°F.

TABLE IV

MARK I ELECTROLYTIC PRETREATMENT CELL PERFORMANCE SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Overall Time Average Cell Voltage volts	Period Overall Time Average Cell Current amps	Period Overall Time Average Anode Current Density mA/cm^2	Period Watt-Hour Input per Pound of Water(2) wh/lb	Period Faradays Required per Mole of TKN(1) F/n	Period Overall Time Average Watt-Hour Input per Pound of Water(2) Required to Remove 1.0 g TKN(1)/ℓ wh/lb g/ℓ
7062801 18.0 Hours	None 6.76 - 6.64	Constant 1.90	0.0704	0.367	3.11	15.7	25.9
7070601 12.0 Hours	Added #7765 Catalyst at 1.23 g/lb. 6.64 - 6.34	Constant 1.90	0.193	1.01	5.99	12.1	20.0
7072401 14.83 Hours	Added #8111 Catalyst at 1.20 g/lb. 6.25 - 5.92	Constant 1.90	0.114	0.413	3.80	6.97	11.5
7080901 12.0 Hours	Added #7765 Catalyst at 1.20 g/lb. 6.25 - 6.12	Constant 1.90	0.158	0.570	4.25	19.8	32.7

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.

(2) This value is based on the actual volume of the urine being processed, where it is assumed that each liter of urine at any stage in the electrolytic pretreatment process contains 2.20 pounds of water at 75°F.

TABLE V

MARK I ELECTROLYTIC PRETREATMENT CELL PERFORMANCE SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Overall Time Average Cell Voltage volts	Period Overall Time Average Cell Current amps	Period Overall Time Average Anode Current Density mA/cm^2	Period Watt-Hour Input per Pound of Water(2) wh/lb	Period Faradays Required per Mole of TKN(1) F/n	Period Overall Time Average Watt-Hour Input per Pound of Water(2) Required to Remove 1.0 g TKN(1)/ℓ wh/lb g/ℓ
7090701 20.0 Hours	None 6.650 - 6.185	Constant 1.90	0.0636	0.229	2.76	3.57	5.93
7091101 9.0 Hours	(3) 6.185 - 5.705	Constant 1.90	0.0493	0.178	1.28	1.61	2.66
7091301 21.17 Hours	Added #7765 Catalyst at 0.10 g/lb. 6.65 - 6.17	Constant 1.90	0.0366	0.132	1.69	2.11	3.52
7091501(5) 9.17 Hours	Adjusted pH with NaOH from 7.45 to 8.45. 6.02 - 6.02(4)	Constant 1.90	0.0710	0.256	1.83	(4)	(4)
7091802 18.17 Hours	Added $NiCl_2$ Catalyst at 0.10 g/lb. 6.65 - 6.29	Constant 1.90	0.0308	0.111	1.22	2.03	3.38

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.
(2) This value is based on the actual volume of the urine being processed, where it is assumed that each liter of urine at any stage in the electrolytic pretreatment process contains 2.20 pounds of water at 75°F.
(3) Maintained pressure above urine at gas-liquid separator at 1/2 to 2/3 atmosphere and maintained urine temperature at 65°F where ambient temperature was 75°F.
(4) No measurable Total Kjeldahl Nitrogen was removed after 9 hours of cell operation.
(5) A very slight amount of ammonia vapor detected at start and end of experiment.

TABLE VI

MARK I ELECTROLYTIC PRETREATMENT EXPERIMENTAL SUMMARY

Experiment No. and Number of Anode/Cathode Electrodes Used	Electrode Materials Used in Cell During Experiment Anodes/Cathodes	Electrode Spacing inches —and— Anode Area cm^2	Electrode Separators Used	Urine Composite No. Used —and— Urine Stabilized With	Volume of Urine Used in Experiment mℓ	Urine Flow Rate through the Cell mℓ/min.	Type of Gas-Liquid Separation Used R = Rapid Separation D = Delayed Separation and Total Gas Pressure
7060701 8/8	A = Platinized Pt with Ni Leads C = Platinized Pt with Ni Leads	0.042 319.8	None. 0.037" VEXAR(1) screen spacer used.	7060710 50 ppm ROCCAL(2)	500	833	R 1 Atm.
7060802 8/8	" " " "	"	"	"	450	"	R 1 Atm.
7061202 8/8	" " " "	"	"	"	400	"	R 1 Atm.
7062801 5/5	A = Platinized Pt with Pt Leads C = Platinized Pt with Pt Leads	0.062 191.9	None. 0.055" VEXAR screen spacer used.	7062710 50 ppm ROCCAL	352	"	D 1 Atm.
7070601 5/5	" " " "	"	"	"	332	"	D 1 Atm.
7072401 7/7	" " " "	0.048 277.2	None. 0.037" VEXAR screen spacer used.	"	385	1400	D 1 Atm.
7080901 7/7	" " " "	"	"	"	385	"	D 1 Atm.
7090701 7/7	" " " "	"	"	7081710 50 ppm ROCCAL	400	833	R 1 Atm.
7091101 7/7	" " " "	"	"	"	300	"	R 1/2 to 2/3 Atm.
7091301 7/7	" " " "	"	"	"	400	"	R 1 Atm.
7091501 7/7	" " " "	"	"	"	307.6	"	R 1 Atm.
7091802 7/7	" " " "	"	"	"	400	"	R 1 Atm.

(1) Supplied by Film Department, E.I. Du Pont De Nemours & Co., Inc.
(2) Supplied as 50% aqueous solution by Sterwin Chemicals, Inc., subsidiary of Sterling Drug , Inc.

TABLE VII

MARK I ELECTROLYTIC PRETREATMENT EXPERIMENTAL RESULTS SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN[1] Concentration g/ℓ	Period Urine pH Change Initial	Final	Period Urine Chloride Change Initial	Final as g/ℓ NaCl	Period Urine Specific Conductivity Change Initial	Final μmho-cm^{-1}	Total Volume of Gases Collected Liters at 24°C and 76cm Hg	Composition of Gases Collected as Analyzed by Gas Chromatography[2]
7060701	None	6.80		8.00		–		0.655	31.8% H_2[3]
11.2	6.34 – 5.68	8.90		7.40		–			53.0% N_2 15.2% O_2
7060802	Added #7765 Catalyst at 1.21 g/lb	8.90		8.91		–		0.150	27.6% H_2[3]
11.2 Hours	5.68 – 4.60	9.00		6.98		–			58.4% N_2 14.0% O_2
7061202	Added $FeCl_3$ Catalyst at 0.068 g/lb	9.00		7.14		–		0.110	17.9% H_2[3]
12.5 Hours	4.60 – 3.27	8.90		5.16		11,900			67.8% N_2 14.3% O_2
7062801	None	6.60		7.56		17,000		0.554	63.2% H_2
18.0 Hours	6.76 – 6.64	8.45		7.22		16,000			25.5% N_2 11.3% O_2
7070601	Added #7765 Catalyst at 1.23 g/lb	8.45		8.76		–		0.611	81.8% H_2
12.0 Hours	6.64 – 6.34	6.95		8.74		17.200			16.1% N_2 2.1% O_2
7072401	Added #8111 Catalyst at 1.20 g/lb	6.80		9.13		17.750		0.402	(4)
14.83 Hours	6.25 – 5.92	6.78		8.00		16,000			
7080901	Added #7765 Catalyst at 1.20 g/lb	6.80		9.06		17,750		0.317	(4)
12.0 Hours	6.25 – 6.12	7.60		8.48		18,500			
7090701	None	6.48		7.36		17,000		0.320	71.7% H_2
20.0 Hours	6.650 – 6.185	7.72		7.10		16,000			24.3% N_2 3.5% O_2
7091101	None	7.72		7.10		16,000		(5)	(5)
9.0 Hours	6.185 – 5.705	8.50		6.80		15 500			
7091301	Added #7765 Catalyst at 0.10 g/lb	6.48		7.36		17,000		0.199	72.2% H_2
21.17 Hours	6.65 – 6.17	7.45		6.00		15,500			24.3% N_2 3.5% O_2
7091501	pH Adjusted with NaOH	8.45		6.00		15,500		0.194	60.9% H_2
9.17 Hours	6.02 – 6.02	8.62		7.00		15,000			31.3% N_2 7.8% O_2
7091802	Added $NiCl_2$ Catalyst at 0.10 g/lb	6.48		7.36		17,000		0.152	75.6% H_2
18.17 Hours	6.65 – 6.29	7.42		7.16		15,400			21.2% N_2 3.2% O_2

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.

(2) Analyses do not include CO_2 which probably was present.

(3) This composition very much in doubt: low values for H_2 with high values for O_2 indicate gas leakage.

(4) Analysis not made because of gas chromatograph malfunction.

(5) Collection and analysis not performed because hydroaspirator used to reduce the total gas pressure.

Electrochemical oxidation experiments 7060701, 7060802 and 7061202 were conducted to shake-down the complete system and procedure and evaluate the performance of the first laboratory electrolysis cell in a continuously circulating urine flow system. Although several difficulties occurred during the experiments, the results of these preliminary tests indicated that the Mark I cell, the system and the procedures would perform satisfactory. The performance results shown in Table III also indicated that the addition of Astropower #7765 catalyst and $FeCl_3$ catalyst improved the electrochemical efficiency of the cell for removing Total Kjeldahl Nitrogen expressed as Faradays required per mole of TKN. The use of $FeCl_3$ in urine, however, lowers the urine pH and increases the amount of percipitates in the system and its use was therefore discontinued. The constant voltage of 1.90 volts was used in order to remain below excessive water electrolysis.

A slight urine leakage occurred several times during the experiments at the top of the electrolysis cell where the lead terminal bolts were projected through the case cover and at several places around the sealing junction of the top cover and the case. These leaks were repaired as they arose without terminating the runs and while they were sufficiently sealed against liquid leakage, a small continuous gas leakage could not have been as easily detected. This possibility of leakage was then eliminated for the next series of experiments by improving the cover-to-case sealing procedure and by flipping the cell case over so the sealed bottom end was at the top during operation.

The nickel leads to the platinum anode electrodes were appreciably consumed during the first three experiments. Nickel leads were used because all of the available platinum at the time was used in constructing the electrode plates. The nickel leads were removed from the cell and were replaced with platinum leads. The stainless steel terminal bolts for the electrode leads were not attacked and they were retained. The exposed surfaces of the stainless steel terminal bolts were coated with a protective epoxy material, however, to insure continued resistance.

Electrochemical oxidation experiments 7062801, 7070601, 7072401 and 7080901 were conducted to evaluate the effects of increasing the spacing distance between electrodes and increasing the urine flow rate through the cell. The results are shown in Table IV.

The efficiency of the electrochemical oxidation was found to decrease markedly with a change in electrode spacing from 0.042 to 0.062 inch. It is believed that this marked decrease may not be due to only electrode spacing change. The cell was disassembled after experiment 7070601 had been completed and inspection revealed that during cell operation poor electrical connection could have developed for a number of the individual electrode leads. If this actually happened, a lower voltage was applied to the electrodes due to high resistance drop across the faulty connections.

The results of experiments 7060701 through 7070601 had previously indicated that an increase in electrode spacing from 0.042 to 0.062 inch caused a significant increase in the power requirement. This apparent

effect of electrode spacing was also in doubt because of possible poor electrical connection for a number of individual electrode leads. On the basis that this apparent effect of electrode spacing was real, it was postulated that a higher degree of anode-cathode solution mixing would give higher electrochemical efficiency, since the urine flow rates were the same for both electrode spacings. The results of experiments 7072401 and 7080901, however, did not agree with this postulate and appear to indicate that electrode spacing and degree of agitation have separate effects on the electrochemical oxidation efficiency.

Electrochemical oxidation experiments 7090701, 7091101, 7091301, 7091501 and 7091802 were the last series of tests conducted with the Mark I cell to obtain design criteria for scaling up to the larger and more complex Mark II cell and system. The results of the last Mark I cell experiments are shown in Table V.

The objective of the last series of experiments was to determine what was mainly responsible for the marked difference in the cells performance between the first two experiments (7060701 and 7060802) and the next four experiments 7062801 through 7080901). The results of these six experiments also did not appear conclusive about the effects of electrode spacing and degree of agitation (urine flow rate through the cell). The last five experiments (7090701 through 7091802) were therefore designed to duplicate as nearly as possible the same experimental conditions that were imposed in the first two experiments.

The urine circulating loop was the same as with the previous experiments except the delayed gas-liquid separation tube was replaced with the rapid gas-liquid separation tube. These gas-liquid separation tubes are explained as follows.

The electrolysis cell effluence in the continuously circulating urine flow system flows up vertically for 3 inches into a tee fitting. (The helium purging gas is introduced at this tee.) From the tee, the cell effluence flows horizontally for 11 inches through vinyl tubing, over and down into a glass tube leading into the top section of the 500 ml dispensing-burette urine reservoir vessel. So far, two distinct glass tubes, each having a 90^{o} bend at the very bottom, were used — one very short tube, and one long tube. The short tube — the rapid gas-liquid separator — causes the electrolysis cell effluence to impinge on the reservoir vessel inside wall 2 to 5 inches above the reservoir urine liquid surface. The cell effluence fans out on the wall presenting a large liquid surface to the gas phase as it flows down and into the liquid phase. The long tube — the delayed gas-liquid separator — continues down to conduct the electrolysis cell effluence 5 to 6 inches below the reservoir urine liquid surface. The gases generated in the urine by the cell are thus well mixed into the reservoir urine and are in contact with this urine for a longer period of time.

The top of the 500 ml dispensing-burette urine reservoir vessel also contains another very short glass tube used to conduct the generated gases

over into the gas collection and gas volume measuring system. During the one special experiment where reduced pressure was used to enhance a more rapid escape of gases from the cell effluence with the rapid gas-liquid separator, this gas collection tube was disconnected from the gas collection system and connected to a vacuum system. The vacuum system consisted of a water aspirator pump, a pump water-backflow trap, a needle valve, a 90-cm mercury filled manometer and another water trap between the manometer and the gas collection tube.

The impingement type rapid gas-liquid separator used in the first two experiments was used in all five present experiments. The delayed gas-liquid separator was installed because at the time it was thought that a longer dwell time for the reactants would prove beneficial to the cell's performance. Experiment 7091101 was designed to amplify the rapid gas-liquid separation factor to further examine its effect. The same Astropower 7765 catalyst evaluated in the first two experiments was again evaluated except that the concentration was reduced. Since the urine pH changed from 6.80 to 8.90 for experiment 7060701 and from 8.90 to 9.00 for experiment 7060802, experiment 7091501 was included to see if the high pH was responsible for the better performance. And finally, even though nickel is not mentioned in the catalyst column of Table III for the first three experiments, nickel was definitely in the urine solution in each case some time during the cell's operation because the nickel anode leads were appreciably consumed during these experiments. Experiment 7091802 was included to see if nickel in solution was responsible for the better performance.

It would appear from a comparison among all the experimental results obtained that the effect of rapid gas-liquid separation on the power requirement is to reduce the requirement considerably over that required where delayed gas-liquid separation is used. The only result that did not fit neatly into the design of the experiments is that of experiment 7091501 where the urine pH was increased. This is also the first time that a very slight amount of ammonia vapor had been detected over the urine during these experiments.

Mark II Cell Experiments. — The results of the Mark II operational performance experiments are shown in Tables VIII and IX. These tables show the cell experimental operating parameters, the constant voltage imposed and the periodic performance values obtained. The cell as operated continuously under a reduced pressure and the gases generated were scrubbed, collected and analyzed for their composition. Summaries of the Mark II experimental conditions and results are shown in Tables X and XI.

The results obtained during long duration experiment 8022201 (Table VIII), conducted at a constant 1.90 volts, show a marked reduction in the average rate of Total Kjeldahl Nitrogen removal and a noticeable drop in overall time average current density compared with the values obtained operating the Mark I cell at this same voltage. Low electrochemical efficiencies were also obtained among the four periods of the long experiment. In addition, the pH of the urine increased to a fairly high value during the first 23-hour period and free ammonia was detected in the urine from this point on. The

TABLE VIII

MARK II ELECTROLYTIC PRETREATMENT CELL PERFORMANCE SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Overall Time Average Cell Voltage volts	Period Overall Time Average Cell Current amps	Period Overall Time Average Anode Current Density mA/cm^2	Period Watt-Hour Input per Pound of Water(2) wh/lb	Period Faradays Required per Mole of TKN(1) F/n	Period Overall Time Average Watt-Hour Input per Pound of Water(2) Required to Remove 1.0 g TKN(1)/ℓ wh/lb g/ℓ
8022201(3) 23.25 Hours	Added #7765 Catalyst at 0.10 g/lb. 7.483 - 7.416	Constant 1.90	0.0495	0.0600	0.995	8.97	14.9
8022201(3) 72.75 Hours	None 7.416 - 7.356	Constant 1.90	0.0241	0.0293	1.59	16.0	26.6
8022201(3) 71.0 Hours	None 7.356 - 7.267	Constant 1.90	0.0178	0.0215	1.21	8.18	13.5
8022201(3) 93.0 Hours	None 7.267 - 7.210	Constant 1.90	0.0175	0.0212	1.70	17.5	29.8
8022201 Overall Totals 260 Hours	3.65% TKN Removed	Constant 1.90	–	–	5.49	–	20.1

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.
(2) This value is based on the actual volume of the urine being processed, where it is assumed that each liter of urine at any stage in the electrolytic pretreatment process contains 2.20 pounds of water at 75°F.
(3) Slight amount of free ammonia vapor detected at end of each operational period.

TABLE IX

MARK II ELECTROLYTIC PRETREATMENT CELL PERFORMANCE SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Overall Time Average Cell Voltage volts	Period Overall Time Average Cell Current amps	Period Overall Time Average Anode Current Density mA/cm^2	Period Watt-Hour Input per Pound of Water(2) wh/lb	Period Faradays Required per Mole of TKN(1) F/n	Period Overall Time Average Watt-Hour Input per Pound of Water(2) Required to Remove 1.0 g TKN(1)/ℓ wh/lb g/ℓ
8030901 72.0 Hours	Added #7765 Catalyst at 0.10 g/lb. 7.49 - 7.08	Constant 2.12	0.108	0.131	7.50	9.86	18.3
8030901 72.0 Hours	None 7.08 - 6.88	Constant 2.14	0.0989	0.120	7.30	19.9	37.0
8030901 72.0 Hours	None 6.88 - 6.34	Constant 2.16	0.0753	0.0912	5.91	5.79	10.9
8030901 66.0 Hours	None 6.34 - 6.16	Constant 2.16	0.0562	0.0681	4.28	12.7	23.9
8030901 72.0 Hours	None 6.16 - 5.89	Constant 2.18	0.0577	0.0699	5.13	10.0	18.9
8030901 72.0 Hours	None 5.89 - 5.63	Constant 2.06	0.0295	0.0358	2.67	5.78	10.4
8030901 69.9 Hours	Brought #7765 Catalyst Loading up to 1.2 g/lb. 5.63 - 3.45	Constant 2.16	0.448	0.543	44.2	10.7	20.2
8030901 71.0 Hours	Adjusted pH with NaOH from 5.05 to 7.95. 3.45 - 1.73	Constant 2.16	0.104	0.126	16.5	5.12	9.62
8030901 71.4 Hours	Adjusted pH with H Cl from 6.55 to 5.98. 1.73 - 0.535	Constant 2.16	0.137	0.167	22.6	10.0	18.9
8030901 Overall Totals 638.3 Hours	92.9% TKN Removed	–	–	–	116.1	–	16.7

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.

(2) This value is based on the actual volume of the urine being processed, where it is assumed that each liter of urine at any stage in the electrolytic pretreatment process contains 2.20 pounds of water at 75°F.

TABLE X

MARK II ELECTROLYTIC PRETREATMENT EXPERIMENTAL SUMMARY

Experiment No. Period, and Number of Anode/Cathode Electrodes Used	Electrode Materials Used in Cell During Experiment Anodes/Cathodes	Electrode Spacing inches —and— Anode Area cm^2	Electrode Separators Used	Urine Composite No. Used —and— Urine Stabilized With	Volume of Urine Used in Experiment mℓ	Urine Flow Rate through the Cell mℓ/min.	Type of Gas-Liquid Separation Used R = Rapid Separation D = Delayed Separation and Total Gas Pressure
8022201 First Period 10/11	A = Platinized Pt with Pt Leads C = type 316 SS with type 347 SS Leads	0.048 825.2	Yes. 0.0025" DYNEL plus(1) ASAHI Screen	8021610 50 ppm ROCCAL(2)	1000	833	R 1/3 to 2/3 Atm.
" Second Period	" "	"	"	"	953	"	" "
" Third Period	" "	"	"	"	904	"	" "
" Fourth Period	" "	"	"	"	855	"	" "
8030901 First Period 10/11	" "	"	"	8021610 50 ppm ROCCAL	1000	833	R 1/3 to 2/3 Atm.
" Second Period	" "	"	"	"	950	"	" "
" Third Period	" "	"	"	"	900	"	" "
" Fourth Period	" "	"	"	"	850	"	" "
" Fifth Period	" "	"	"	"	800	"	" "
" Sixth Period	" "	"	"	"	750	"	" "
" Seventh Period	" "	"	"	"	700	"	" "
" Eigth Period	" "	"	"	"	437	"	" "
" Ninth Period	" "	"	"	"	427.5	"	" "

(1) WEBRIL #M1401 supplied by Fiber Products Division, The Kendall Company.
(2) Supplied as 50% aqueous solution by Sterwin Chemicals Inc., Subsidiary of Sterling Drug Inc.

TABLE XI

MARK II ELECTROLYTIC PRETREATMENT EXPERIMENTAL RESULTS SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Urine pH Change Initial – Final	Period Urine Chloride Change Initial – Final as g/ℓ Na Cℓ	Period Urine Specific Conductivity Change Initial – Final μmho-cm^{-1}	Cumulative Total Weight of CO_2 Gas Collected in Gas Scrubber g	Period Volume of Gases Collected Liters at 24°C and 76 cm Hg	Composition of Gases Collected as Analyzed by Gas Chromatography
8022201	Added #7765 Catalyst at 0.10 g/lb.	6.30	9.24	20,500	0	2.305	4.6% H_2 79.5% N_2
23.25 Hours	7.483 - 7.416	8.85	9.30	31,000			15.9% O_2
"	None	8.85	9.30	31,000	(2)	4.583	5.9% H_2 79.7% N_2
72.75 Hours	7.416 - 7.356	8.85	9.32	34,000			14.4% O_2
"	None	8.85	9.32	34,000	(2)	6.030	6.8% H_2 77.2% N_2
71.0 Hours	7.356 - 7.267	8.86	9.24	34,200			16.0% O_2
"	None	8.86	9.24	34,200	1.51	5.645	5.5% H_2 74.8% N_2
93.0 Hours	7.267 - 7.210	8.80	9.40	34,000			19.7% O_2
8030901	Added #7765 Catalyst at 0.10 g/lb.	6.30	9.18	19,500	0	5.992	36.3% H_2 50.3% N_2
72.0 Hours	7.49 - 7.08	6.75	9.20	17,500			13.4% O_2
"	None.	6.75	9.20	17,500	(2)	5.228	37.8% H_2 48.4% N_2
72.0 Hours	7.08 - 6.88	7.02	9.20	19,900			13.8% O_2
"	None.	7.02	9.20	19,900	(2)	4.134	38.8% H_2 47.6% N_2
72.0 Hours	6.88 - 6.34	7.00	9.12	19,700			13.6% O_2
"	None.	7.00	9.12	19,700	(2)	2.785	32.8% H_2 52.1% N_2
66.0 Hours	6.34 - 6.16	7.14	9.16	22,000			15.1% O_2
"	None.	7.14	9.16	22,000	(2)	3.785	31.5% H_2 52.0% N_2
72.0 Hours	6.16 - 5.89	7.42	9.18	21,500			16.5% O_2
"	None.	7.42	9.18	21,500	(2)	2.270	25.6% H_2 57.2% N_2
72.0 Hours	5.89 - 5.63	7.45	9.22	20,600			17.2% O_2
"	Brought #7765 Catalyst loading up to 1.2 g/lb.	7.45	9.22	20,600	(2)	7.280	62.9% H_2 32.5% N_2
69.9 Hours	5.63 - 3.45	5.05	10.00	21,400			4.6% O_2
"	Adjusted pH with NaOH from 5.05 to 7.95	7.95	10.00	21,400	14.22	3.860	61.0% H_2 33.0% N_2
71.0 Hours	3.45 - 1.73	6.55	(2)	21,900			6.0% O_2
"	Adjusted pH with H Cℓ from 6.55 to 5.98	5.98	(2)	21,900	15.62	4.165	(4)
71.4 Hours	1.73 - 0.535	7.05 (3)	9.78	26,800			

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.
(2) Analysis not performed.
(3) This is the measured value of the pH after 41 hours of cell operation, final value not obtainable.
(4) Analysis not made because of Gas Chromatograph malfunction.

sodium hydroxide gas scrubbing solution and the water in the gas collecting system were analyzed for an increase in Total Kjeldahl Nitrogen content (from free ammonia gas carryover) at the end of the experiment. No increase in Total Kjeldahl Nitrogen was found. The sodium hydroxide gas scrubbing solution was also analyzed for an increase in chloride content (from possible free Cl_2 gas carryover) and no increase was found. The sodium hydroxide gas scrubbing solution at the end of the experiment was found to have collected 1.51 grams of CO_2 gas.

A polarization curve of current obtained versus applied voltage was measured near the termination of this long experiment. The polarization curve showed a break at 2.16 volts so it was decided to initiate another long duration experiment and operate the cell at various voltage settings around 2.16 volts. The cell was dismantled, inspected and cleaned thoroughly before starting the next experiment. No change or damage was observed in the cell or the stainless steel electrodes.

The results of long-duration experiment 8030901 conducted with the Mark II cell are shown in Table IX. The organic nitrogen content of the urine in this experiment, as determined by Total Kjeldahl Nitrogen analysis, was reduced from 7.49 to 0.535 grams per liter. The sodium hydroxide gas scrubbing solution was analyzed for an increase in chloride content (from possible free Cl_2 gas carryover) at the end of the eighth and ninth (final) operational periods. Since the pH was adjusted to the acid side for the ninth period, it was felt that this period should be especially monitored. No increase in chloride content was found at the ends of either period. The sodium hydroxide gas scrubbing solution at the ends of the eighth and ninth operational periods was found to have collected 14.22 and 15.62 grams of CO_2 gas respectively.

The conclusions from the results of long-duration experiment 8030901 are as follows:

1. Operating the electrolytic pretreatment cell at a reduced pressure does not appear to offer any substantial increase in performance over operation at ambient total pressure. This conclusion is shown when the performance results in Table XIII, where the Total Kjeldahl Nitrogen concentration is above 0.5 g/l, is compared with the performance results in Table IX. Perhaps, reduced pressures do not significantly affect the rate of gas-liquid separation.
2. Increasing the Astropower 7765 catalyst loading from 0.10 to 1.2 grams per pound of urine increased the rate of Total Kjeldahl Nitrogen removal by a factor of 4 to 5. This conclusion is shown in Table IX and Figure 17 when the amount of nitrogen removed in the first six 72-hour periods is compared with the nitrogen removal rate in the last three 72-hour periods. The power efficiency does not appear to be significantly affected.

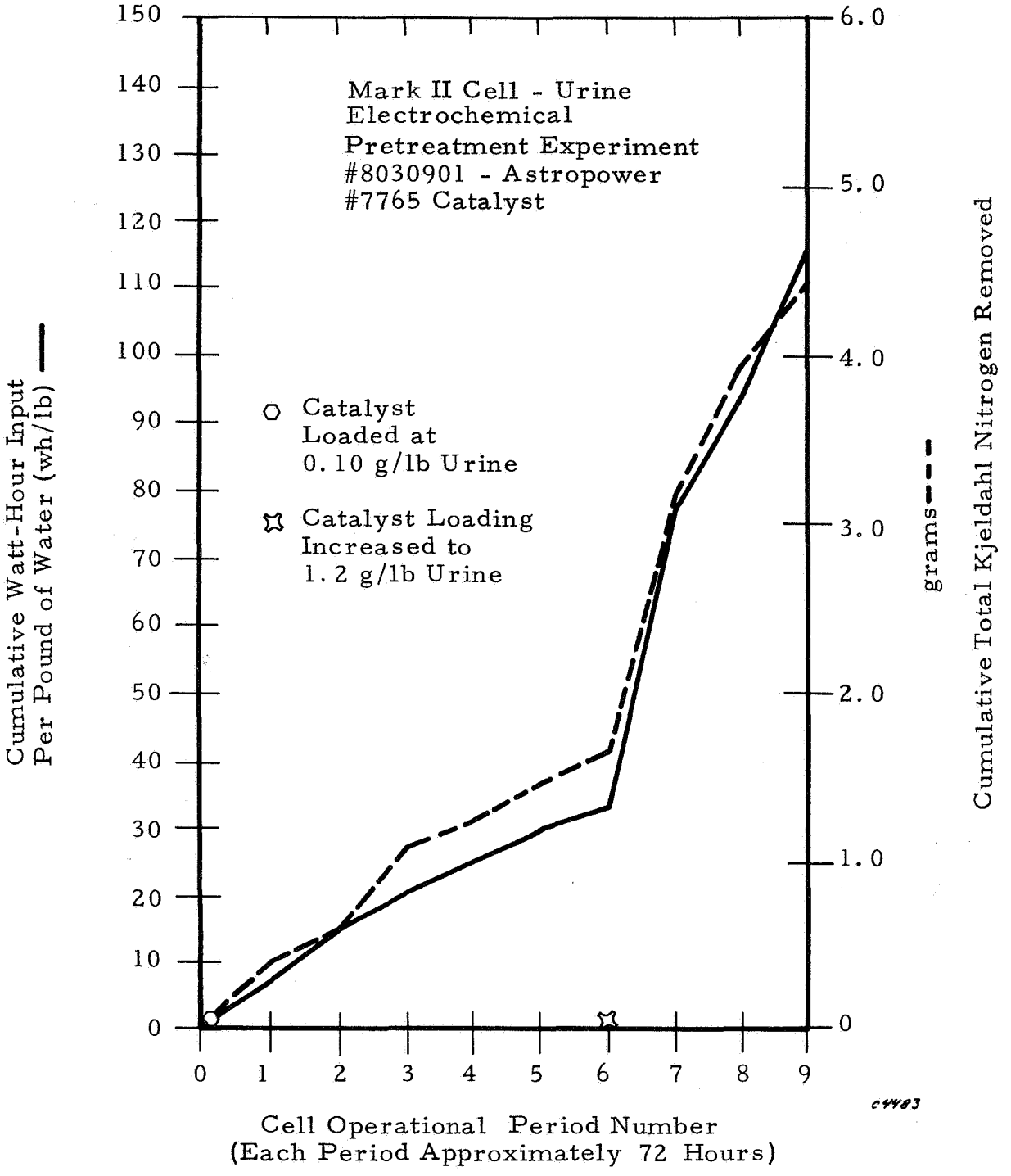

Figure 17. Catalyst Loading Effect on Watt Hour Input and Rate of Total Kjeldahl Nitrogen Removal.

3. Operating the cell with the Astropower 7765 catalyst where the pH of the urine is between 7 and 8 appears to offer better performance than when the urine pH is between 5 and 6. This conclusion is shown when the pH values listed in Table XI are compared with the performance values listed in Table IX. The last three period test results in Table IX also appear to indicate that the cell current density is reduced for the same operating voltage when the pH is raised anywhere within the range of 5 to 8.

4. The electrolytic pretreatment of urine removes other organic material from urine in addition to Kjeldahl organic nitrogen. This conclusion is suggested when the Faraday and power efficiencies are compared over the first six 72-hour periods. These values seem to vary in an irregular manner. This vacillation in performance has been noted in most of the other periodically conducted tests. This consistent variation of data indicates the difficulty in trying to obtain a correct performance test conclusion from one or two test periods even though a test period is for three days with the same urine. The Kjeldahl analyses were carefully checked for their accuracy and even though they are not extremely accurate, their variance could not account for these 2 to 3 fold performance variations.

Mark III Cell Experiments. — The results of the Mark III operational performance experiments are shown in Tables XII, XIII, XIV and XV. These tables show the cell experimental operating parameters, the constant current imposed and the periodic performance values obtained. Table XII covers Run I, the initial shakedown test, and it differs from the next three runs in that a 3.5-liter starting volume of urine was used, urea was not added to the raw urine, and a constant current was not imposed throughout the complete run.

The results shown in Tables XIII, XIV, and XV show that the highest performance was obtained by operating the cell at a constant current of 30 amperes compared with 20 or 35 amperes. Urea was added to the raw urine for each of these three runs because most of the composite urine collected here during this program seldom runs higher than 16 g/l urea as determined by Total Kjeldahl Nitrogen analysis where we assume all the Kjeldahl nitrogen is urea. No germicide, such as Roccal, which was added at 50 ppm to the raw urine for all Mark I and Mark II experiments, was used in any of the test with the Mark III cell.

Operating the Mark III cell at a constant current of 30 amperes required 204 Whr per pound of water to reduce the Total Kjeldahl Nitrogen concentration from 9.94 to 0.259 g/l. The results shown in Tables XII and XIII and Figures 18 and 19, clearly show that it becomes increasingly more difficult to remove the Total Kjeldahl Nitrogen as the concentration falls below 0.5 g/l. It is fairly possible that the Kjeldahl nitrogen measured at this concentration and lower is no longer mainly urea and consists mostly of other organic nitrogen species that could be more difficult to remove. Above this concentration, there appears to be no clear trend as to the ease of removing

TABLE XII

MARK III ELECTROLYTIC PRETREATMENT CELL PERFORMANCE SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Overall Time Average Cell Voltage volts	Period Overall Time Average Cell Current amps	Period Overall Time Average Anode Current Density mA/cm²	Period Watt-Hour Input per Pound of Water(2) wh/lb	Period Faradays Required per Mole of TKN(1) F/n	Period Overall Time Average Watt-Hour Input per Pound of Water(2) Required to Remove 1.0 g TKN(1)/ℓ wh/lb g/ℓ
Run I 4.0 Hours	Added #9201 Catalyst at 1.2 g/lb. 5.37 - 2.87	2.89	Constant 30	Constant 1.05	44.1	7.02	17.7
Run I 7.8 Hours	None 2.87 - 0.431	2.96	26.5	0.924	79.1	12.6	32.4
Run I 4.0 Hours	None 0.431 - 0.313	3.09	Constant 30	Constant 1.05	47.9	151	406
Run I 2.0 Hours	None 0.313 - 0.230	3.03	Constant 30	Constant 1.05	23.9	109	288
Run I Overall Totals 17.8 Hours	95.7% TKN Removed	–	–	–	195.0	–	37.9

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.

(2) This value is based on the actual volume of the urine being processed, where it is assumed that each liter of urine at any stage in the electrolytic pretreatment process contains 2.20 pounds of water at 75°F.

TABLE XIII

MARK III ELECTROLYTIC PRETREATMENT CELL PERFORMANCE SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Overall Time Average Cell Voltage volts	Period Overall Time Average Cell Current amps	Period Overall Time Average Anode Current Density mA/cm²	Period Watt-Hour Input per Pound of Water(2) wh/lb	Period Faradays Required per Mole of TKN(1) F/n	Period Overall Time Average Watt-Hour Input per Pound of Water(2) Required to Remove 1.0 g TKN(1)/ℓ wh/lb g/ℓ
Run II 2.0 Hours	Added #9201 Catalyst at 1.2 g/lb. Added urea to urine. 9.94 - 8.82	2.90	Constant 30	Constant 1.05	26.8	9.48	23.9
Run II 2.0 Hours	None 8.82 - 7.20	2.93	Constant 30	Constant 1.05	26.7	6.47	16.5
Run II 3.0 Hours	None 7.20 - 4.75	2.97	Constant 30	Constant 1.05	40.8	6.43	16.6
Run II 2.0 Hours	None 4.75 - 3.11	2.96	Constant 30	Constant 1.05	27.1	6.43	16.5
Run II 2.0 Hours	None 3.11 - 1.31	2.94	Constant 30	Constant 1.05	27.1	5.88	15.0
Run II 2.0 Hours	None 1.31 - 0.413	2.98	Constant 30	Constant 1.05	27.5	11.8	30.7
Run II 2.0 Hours	None 0.413 - 0.259	3.00	Constant 30	Constant 1.05	27.8	69.2	181
Run II Overall Totals 15.0 Hours	97.4% TKN Removed	–	Constant 30	Constant 1.05	203.8	–	21.1

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.

(2) This value is based on the actual volume of the urine being processed, where it is assumed that each liter of urine at any stage in the electrolytic pretreatment process contains 2.20 pounds of water at 75°F.

TABLE XIV

MARK III ELECTROLYTIC PRETREATMENT CELL PERFORMANCE SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Overall Time Average Cell Voltage volts	Period Overall Time Average Cell Current amps	Period Overall Time Average Anode Current Density mA/cm²	Period Watt-Hour Input per Pound of Water(2) wh/lb	Period Faradays Required per Mole of TKN(1) F/n	Period Overall Time Average Watt-Hour Input per Pound of Water(2) Required to Remove 1.0 g TKN(1)/ℓ wh/lb g/ℓ
Run III 3.0 Hours	Added #9201 Catalyst at 1.2 g/lb. Added urea to urine. 12.40 - 11.98	2.76	Constant 20	Constant 0.697	25.5	25.3	60.8
Run III 3.0 Hours	None 11.98 - 11.09	2.51	Constant 20	Constant 0.697	22.9	11.8	25.8
Run III 3.0 Hours	None 11.09 - 9.68	2.54	Constant 20	Constant 0.697	23.3	7.48	16.5
Run III 3.0 Hours	None 9.68 - 8.99	2.52	Constant 20	Constant 0.697	23.2	15.3	33.6
Run III 3.0 Hours	None 8.99 - 8.07	2.51	Constant 20	Constant 0.697	23.2	11.5	25.2
Run III 3.0 Hours	None 8.07 - 6.89	2.55	Constant 20	Constant 0.697	23.6	9.03	20.0
Run III 4.0 Hours	None 6.89 - 5.79	2.51	Constant 20	Constant 0.697	31.1	13.0	28.3
Run III 4.0 Hours	None 5.79 - 4.15	2.53	Constant 20	Constant 0.697	31.0	8.57	18.9
Run III 4.0 Hours	None 4.15 - 2.19	2.72	Constant 20	Constant 0.697	33.3	7.18	17.0
Run III Overall Totals 30.0 Hours	82.3% TKN Removed	–	Constant 20	Constant 0.697	237.1	–	23.2

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.

(2) This value is based on the actual volume of the urine being processed, where it is assumed that each liter of urine at any stage in the electrolytic pretreatment process contains 2.20 pounds of water at 75°F.

TABLE XV

MARK III ELECTROLYTIC PRETREATMENT CELL PERFORMANCE SUMMARY

Experiment No. and Cell Operational Period	Modification of Urine During Experiment and Initial – Final TKN(1) Concentration g/ℓ	Period Overall Time Average Cell Voltage volts	Period Overall Time Average Cell Current amps	Period Overall Time Average Anode Current Density mA/cm²	Period Watt-Hour Input per Pound of Water(2) wh/lb	Period Faradays Required per Mole of TKN(1) F/n	Period Overall Time Average Watt-Hour Input per Pound of Water(2) Required to Remove 1.0 g TKN(1)/ℓ wh/lb g/ℓ
Run IV 2.0 Hours	Added #9201 Catalyst at 1.2 g/lb. Added urea to urine. 12.34 - 11.22	3.06	Constant 35	Constant 1.22	33.0	11.1	29.4
Run IV 2.0 Hours	None 11.22 - 9.50	2.91	Constant 35	Constant 1.22	31.5	7.23	18.3
Run IV 2.0 Hours	None 9.50 - 8.23	2.91	Constant 35	Constant 1.22	31.7	9.82	24.9
Run IV Overall Totals 6.0 Hours	33.3% TKN Removed	–	Constant 35	Constant 1.22	96.2	–	23.4

(1) TKN = Total Kjeldahl Nitrogen by analysis which includes all organically bound nitrogen in the trivalent state plus ammonia nitrogen and using a molecular weight of 14.

(2) This value is based on the actual volume of the urine being processed, where it is assumed that each liter of urine at any stage in the electrolytic pretreatment process contains 2.20 pounds of water at 75°F.

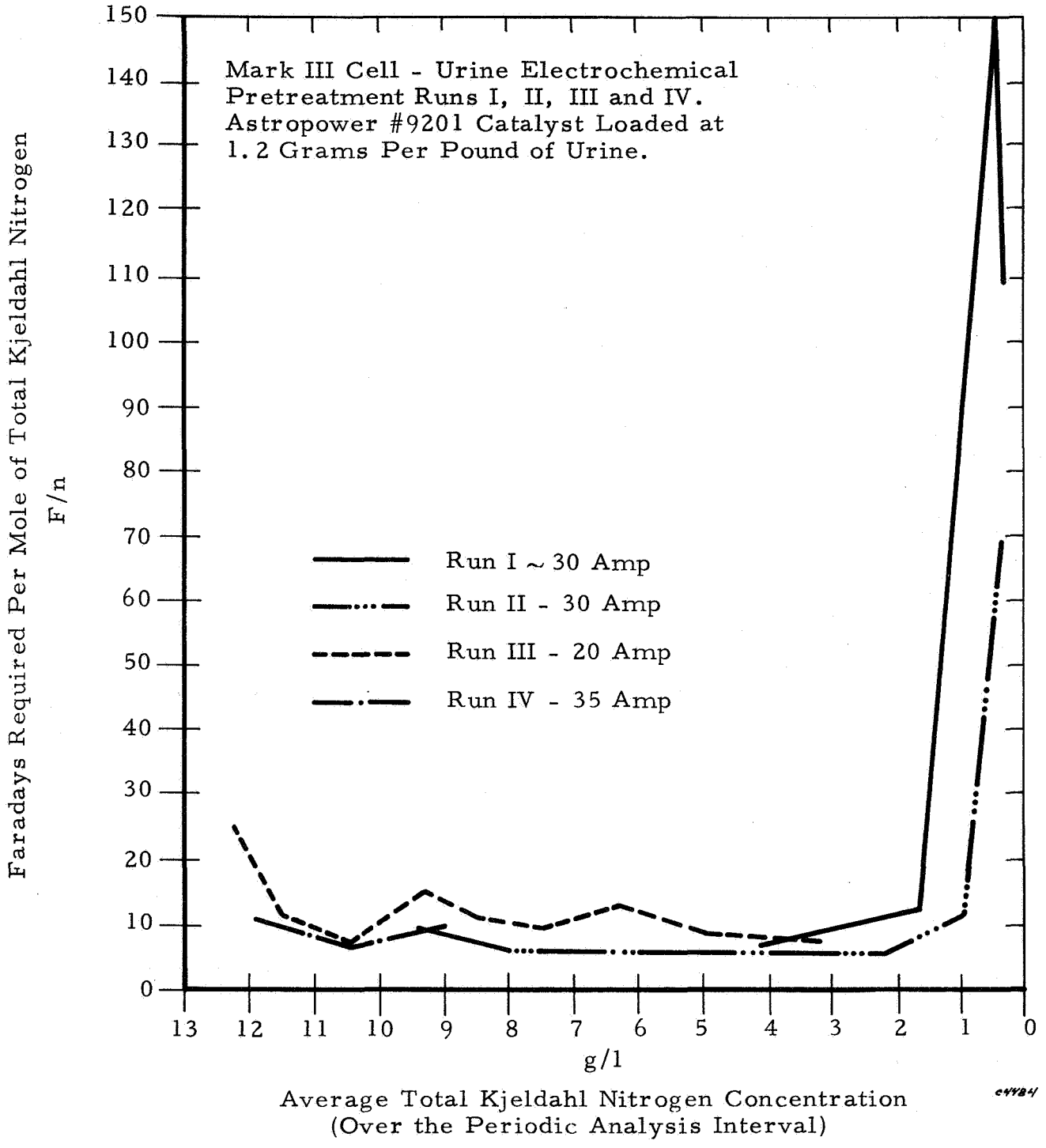

Figure 18. Total Kjeldahl Nitrogen Concentration vs Removal Efficiency

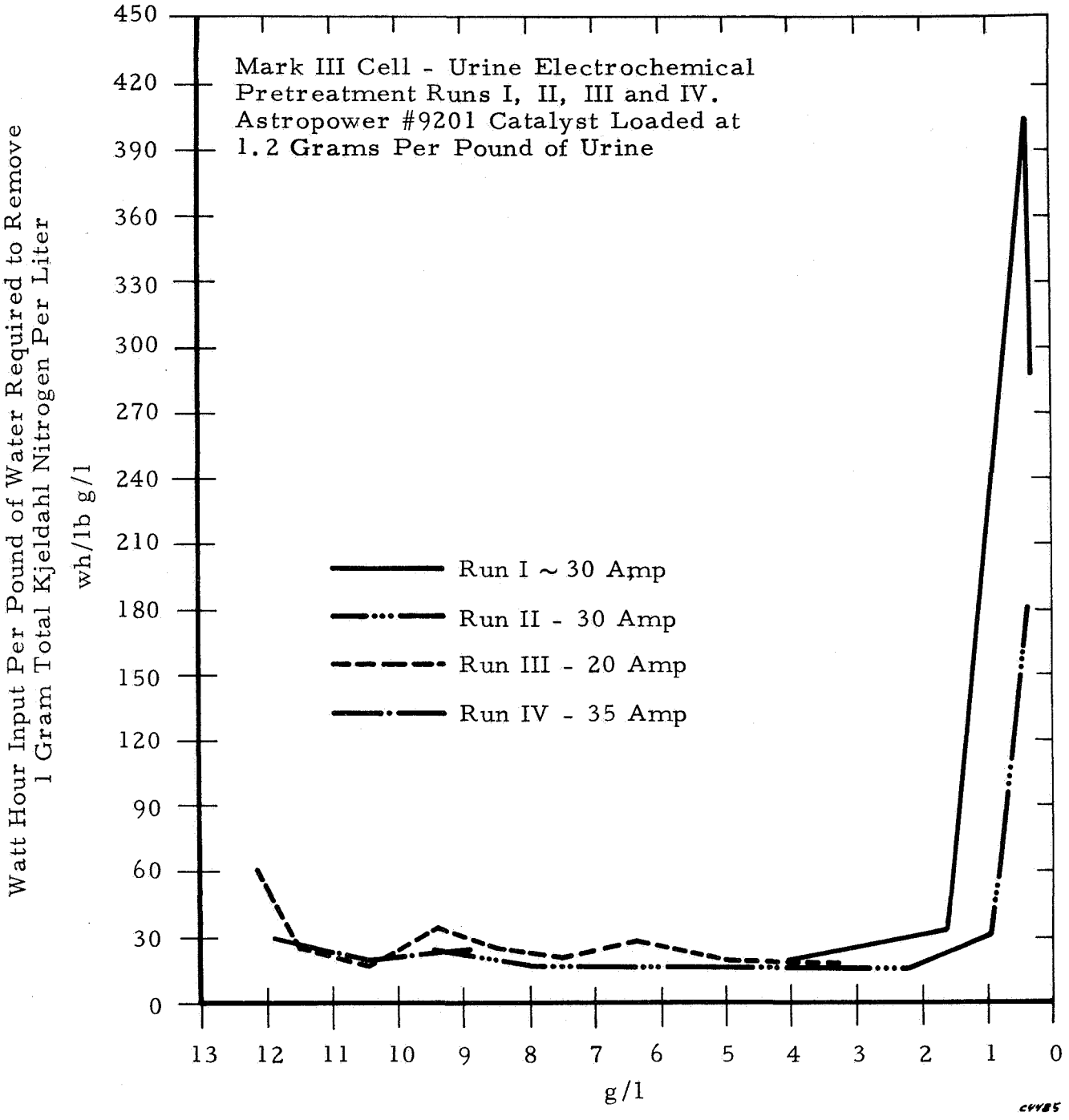

Figure 19. Total Kjeldahl Nitrogen Concentration vs Power Input for Removal

Kjeldahl nitrogen. The electrolyzed product from the first three runs was a clear, almost colorless solution with no observable solids anywhere in the system. The fourth run, Table XV, was terminated on purpose after the short period of cell operation in order to proceed rapidly into the 5-day combined system demonstration test.

The degree of success obtained in scaling up the Mark II cell to the Mark III cell may be examined from one facet by comparing the ratio of the rates at which TKN is removed with the ratio of the platinum anode areas and the amount of catalyst loading. The Mark III cell is almost identical to the Mark II cell in electrode and separator materials and in the use of separators between electrodes to protect the nonplatinum cathode. The platinum anodes were platinized in the Mark II cell and were not platinized in the Mark III cell. The information for making this comparison can be seen by comparing Table XIII with Table IX which is a summary of the results of the last test with the Mark II cell. The Mark III cell removed about 28.75 g TKN using the higher catalyst loading in 15 hours where the Mark II cell removed about 4.44 g TKN in 638 hours. This gives a ratio of rates of removal of about 275 to 1. Since the ratio of platinum anode areas is 34.8 to 1, the Mark III cell performs about 8 times as fast as the Mark II cell with no significant difference in Faraday efficiency or watt-hour input per pound of water. This would appear to suggest that the efficiency of the process does not change much over the current density range of 0.1 to 1mA/cm^2, where the speed of the performance, however, would vary directly with the current density and the catalyst loading.

It is fairly possible that a significant portion of the Kjeldahl organic nitrogen is not urea. It might then be possible that the electrochemical oxidation of the several different species present (or formed) takes place in such a manner as to contribute to the vacillating performance results, which are again noted somewhat in the Mark III cell test results.

A COD analysis performed on the electrolyzed product from Run II with the Mark III cell (Table XIII) indicates a reduction in COD over that for the raw urine of 75 to 80 percent. Since urea is only slightly oxidized in the COD analysis, these results indicate that other organic materials are removed by the electrolytic pretreatment process. If this removal occurs through electrochemical oxidation, this could contribute in the same manner to the vacillating performance results.

Five-Day Run. — In order to simulate actual operating conditions a five-day test was made in which a batch of raw urine plus catalyst (1.2 g/lb urine) was taken down to less than 0.5 g/l of urea, drained and immediately replaced by another batch of catalyzed raw urine. This process was repeated five times. No loss in efficiency or degradation of the Mark III urine pretreatment cell was observed during this entire period. Nor was maintenance of any kind performed on the pretreatment cell during this test. The cell was disassembled at the end of testing and no corrosion or degradation of the electrodes, screens or separators was observed.

The auxiliary system (pumps, sampling, etc.) were not automated for this test and round the clock operations were not attempted. The partly processed urine was stored overnight in the pretreatment cell with no deleterious effects.

Batch size was limited by the urine reservoir gas-liquid separator systems to approximately 3 liters. So for convenience 3-liter bathes were used in each run. Each batch was circulated through the pretreatment cell until the urea content dropped to less than 0.5 g/l. The urea concentration was determined from a Ureometer test. The generally more accurate Kjeldahl nitrogen analyses were also run, but the time required is such that results were not available until the following day. A second indication of urea depletion was the nitrogen content of the evolved gas, as measured by a gas chromatograph. This gas averaged 24% N_2 with the remainder hydrogen and a trace (<1%) oxygen. As the urea in solution became depleted the amount of nitrogen in the evolved gas decreased. This was usually accompanied by an increase in oxygen, Figure 20. It should be noted that this three-to-one ratio of hydrogen to nitrogen is the theoretical composition of the gaseous products of the electrochemical oxidization of urea.

Because the gas evolved during the reaction consisted primarily of the theoretical products of the electrochemical oxidation of urea, nitrogen and hydrogen, the nitrogen gas evolution rate should be a measure of the oxidation rate. To check this hypothesis the total amount of nitrogen gas evolved in each of the five runs was calculated and compared with the amount of nitrogen removed as determined from a Kjeldahl analysis of the solution (see Table XVI).

TABLE XVI

COMPARISON OF NITROGEN EVOLUTION AND KJELDAHL NITROGEN

Run No.	5	6	7	8	9
Nitrogen Gas Evolution (l)	18.7	19.0	15.6	15.3	18.1
Nitrogen Gas Evolution (g)	21.3	21.8	17.8	17.4	20.6
Nitrogen Removed (g) (by Kjeldahl)	20.9	20.0	17.1	16.6	20.2

The current during each run was held constant at 30 amperes except for runs 7, 8 and 9 in which the initial value was 20 amperes for the first 2 to 2-1/2 hours and then 30 amperes for the remainder of the run. This was done to reduce the high initial gassing rate and accompanying foaming.

Run No. 9

Mark III Electrolytic Urine Pretreatment Cell

Input: 6.7 lb raw urine (16 g urea/l)
Output: 6.6 lb product water (<0.5 g urea/l)

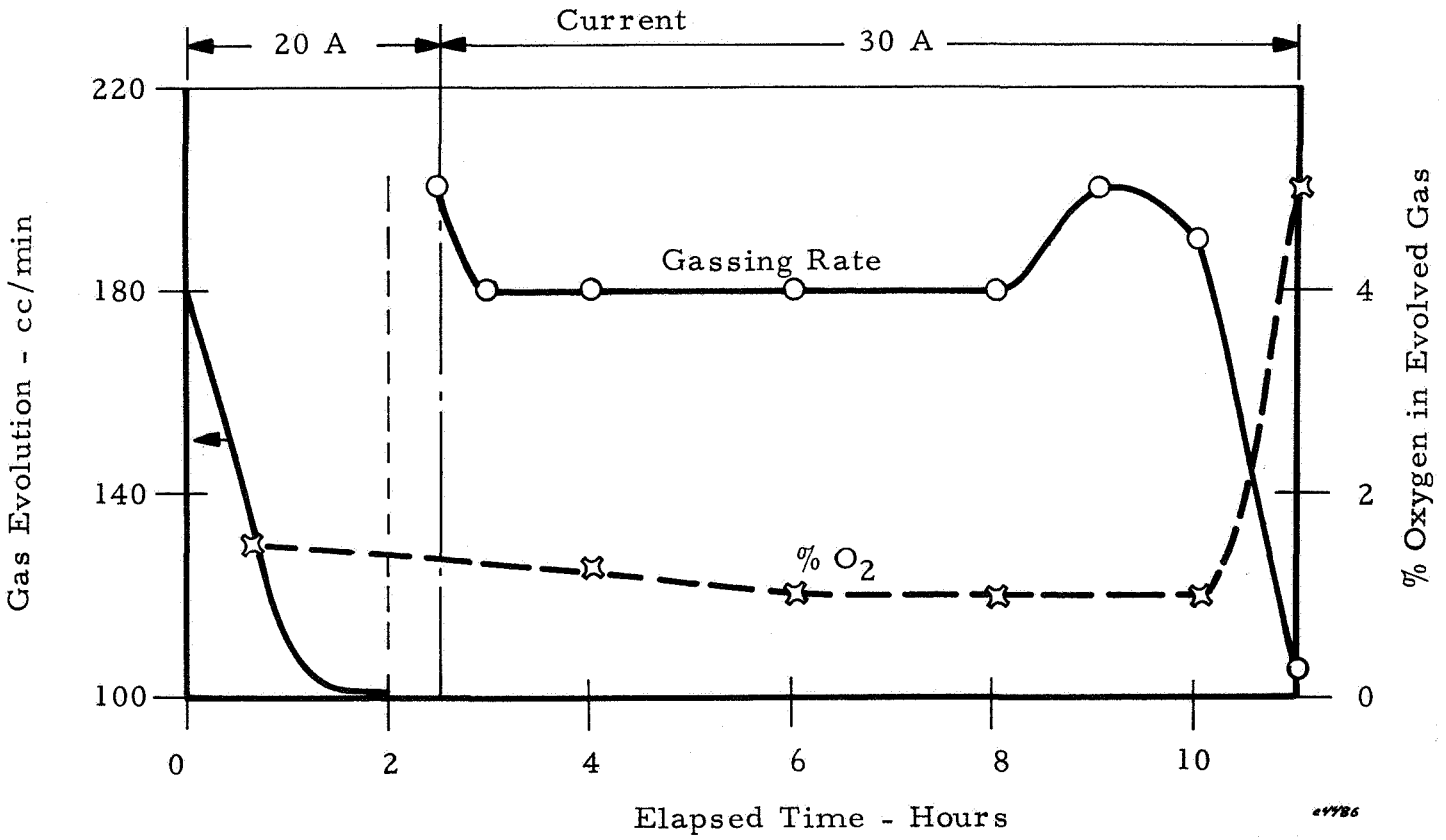

Figure 20. Change in Gas Evolution and Composition During Typical Run

Thus the voltage becomes a measure of the cell resistance. The voltage drop across the cell (and thus the resistance) was found to decrease from 3.3 volts (30 amperes) to 2.65 volts. During this same period the pH dropped from 6.7 to 4.8. Since previous tests (Mark II) had shown best results could be obtained at a pH of 7-8, the pH of the urine was adjusted at this point to approximately 6.7 by adding 8 ml of 50% NaOH (1.84 g NaOH solution/lb urine). The voltage (and cell resistance) immediately climbed to 3.1 volts, but gradually declined again along with the pH to 2.95 volts and a pH of 5.7. The value of voltage and pH then remained constant until near the end of the run when apparently the depletion of urea caused a slight rise to a more neutral pH. These changes are illustrated in a plot of voltage and pH versus time for a typical run (run 6), Figure 21. From this figure it would appear that the relationship between pH and voltage is almost a linear one. In fact, the relationship between the three parameters, voltage, pH and the gas evolution rate, is approximately linear (Figures 22 and 23). Thus to achieve the highest gas evolution and thus the highest rate of urea removal (assuming the gas is nitrogen and hydrogen) it would appear desirable to operate the urine pretreatment cell at the highest voltage, highest pH or both, possible.

To establish this optimum operating voltage more precisely, the gas evolved for each watt-hour of power input (ml/Wh) was calculated and plotted against voltage (Figure 24). At approximately 2.90 volts, a marked increase in the gas evolved per watt hour occurred. It should be noted that this critical voltage is for the cell conditions (flow rate, catalyst, current density, etc.), specified; although it possibly is a basic parameter of the process itself.

At the end of the five-day test a sample of product water was withdrawn from the reservoir of the urine pretreatment system. This sample was placed in a sterile tube and subjected to bacteriological analysis. No bacterial growth in 72 hours was reported, (see Figure 25).

No attempts were made to sterilize the raw urine or any of the pretreatment system. The reservoir was open to the atmosphere before and after each run for loading and draining without any subsequent purging. Thus the electrolytic urine pretreatment process is a self-sterilizing process, probably because of the electrochemical generation of chlorine, hypochlorous acid or free radicals in the pretreatment cell.

The time required to remove the urea from each 3ℓ batch of raw urine varied with the urea concentration and the degree of organic removal. Total removal was not attempted. For comparative purposes the amount of raw urine that could be treated in a 24-hour period was computed. These values and the values of other performance parameters are summarized in Table XVII.

The Total Kjeldahl Nitrogen present in each batch of raw urine was measured initially and at the termination of the run. This difference was divided into the total number of Faradays used during the run to yield an efficiency factor, average value 7.95 F/mole of TKN removed. Power

Run No. 6

Mark III Electrolytic Urine Pretreatment Cell

Constant Current: 30 Amps
Input: 6.7 lb raw urine (17 g urea/l)
Output: 6.6 lb product water (<0.5 g urea/l)

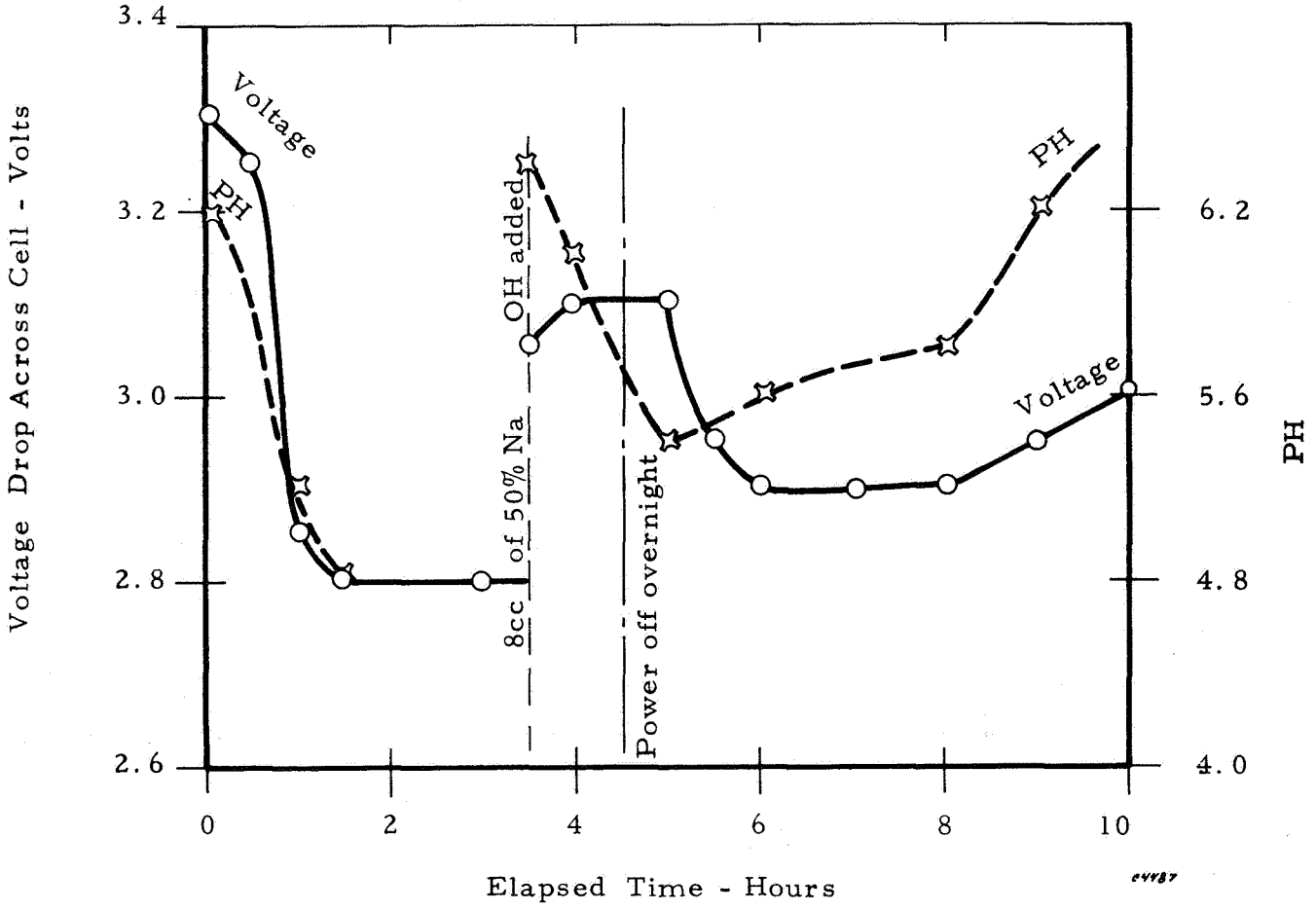

Figure 21. Voltage and pH Change During Typical Run

Run No. 6 Mark III Electrolytic Urine Pretreatment Cell

Constant current: 30 Amps
Input: 6.7 lb raw urine (17 g urea/l)
Output: 6.6 lb product water (<0.5 g urea/l)

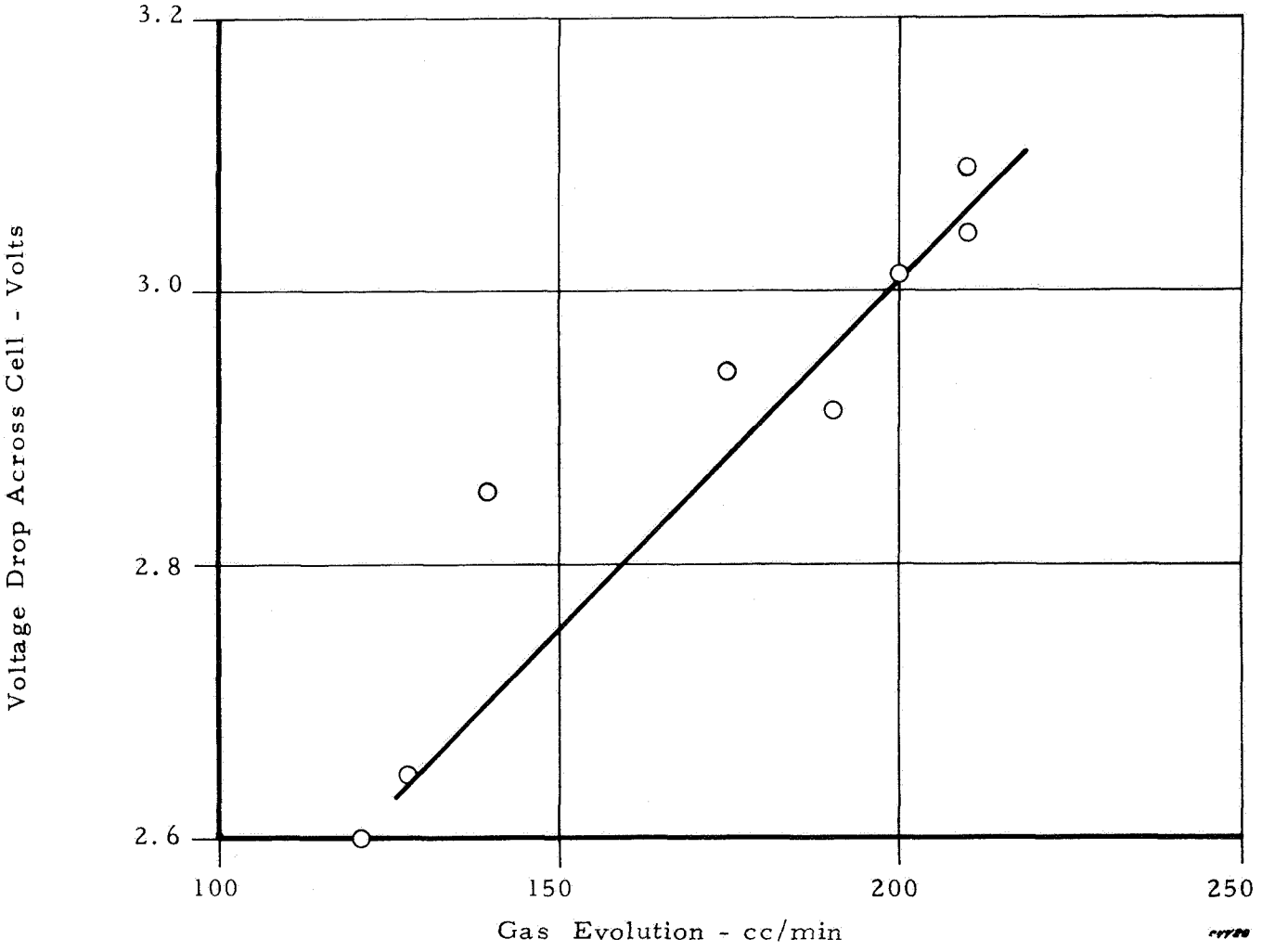

Figure 22. Variation of Gas Evolution Rate With Voltage

Run No. 6

Mark III Electrolytic Urine Pretreatment Cell

Constant current: 30 Amps
Input: 6.7 lb raw urine (17 g urea/l)
Output: 6.6 lb product water (<0.5 g urea/l)

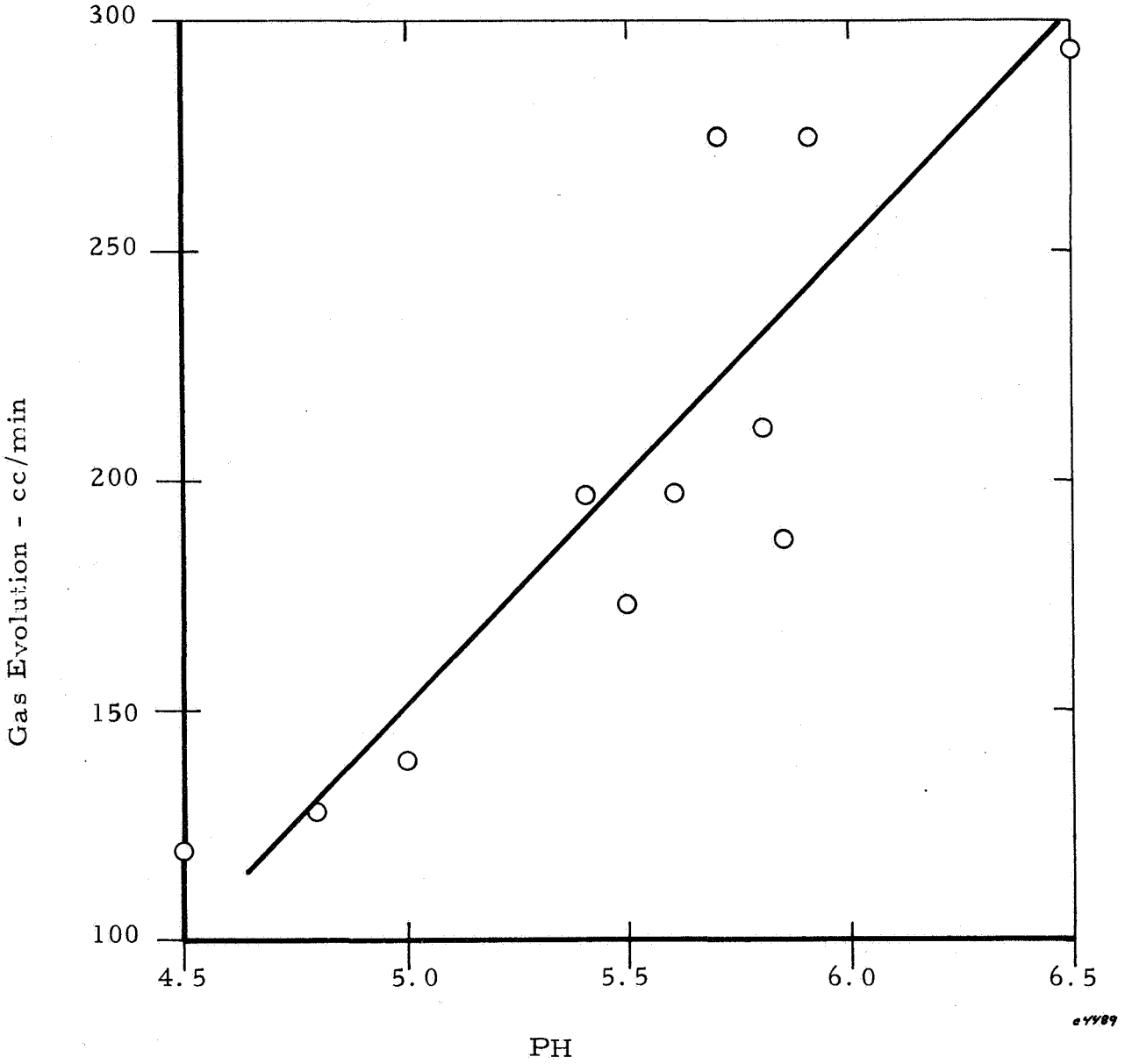

Figure 23. Variation in Gas Evolution Rate with PH.

Run No. 6

Mark III Electrolytic Urine Pretreatment Cell

Input: 6.7 lb raw urine (17 g urea/l)
Output: 6.6 lb product water (<0.5 g urea/l)

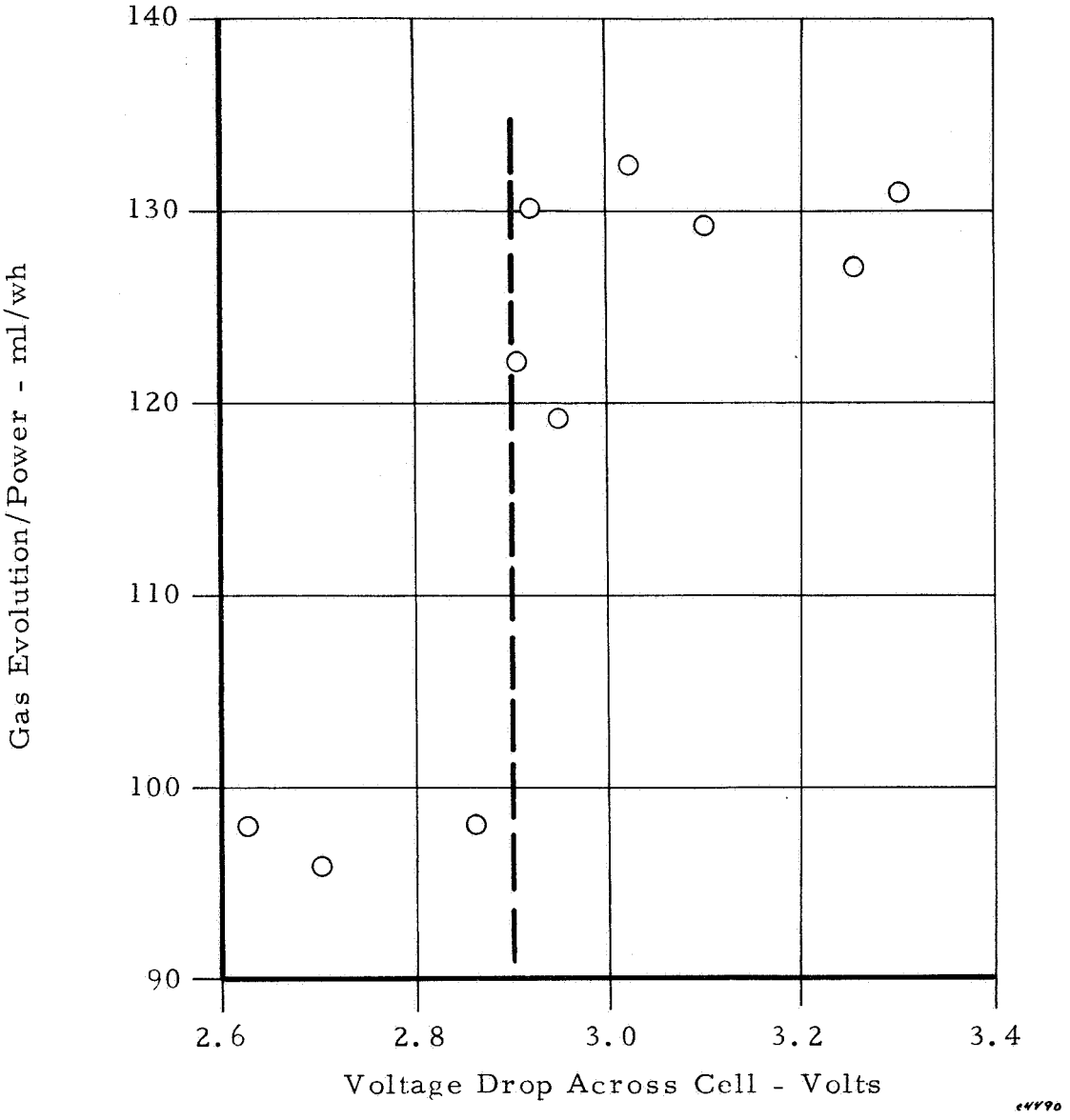

Figure 24. Effect of Cell Voltage on Performance

#1596

CALIFORNIA MICROBIOLOGICAL REFERENCE LABORATORIES

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GARDEN GROVE, CALIFORNIA
PHONE: 534-2661

DIRECTOR Robt. Roaney, M.D.

PATIENT NAME Astropower Water Samples REQUESTING PHYSICIAN T. Heiser

DATE REC'D. 5-22-68 SOURCE Reclaimed water DIAGNOSIS

Specimen # 8052101: Culture and colony count show no growth of aerobic or anaerobic organisms after 72 hours incubation.

Specimen # 8052102: Culture and colony count show no growth of aerobic or anaerobic organisms after 72 hours incubation.

5-24-68 G.H.
GLENN E. HUTCHESON
MICROBIOLOGIST

Figure 25. Laboratory Analysis

TABLE XVII

PERFORMANCE DATA FROM FIVE DAY RUN OF MARK III URINE PRETREATMENT CELL & ELECTRODIALYSIS STACK

Run No.	Run Time (hrs)	Amount of Urine Treated		TKN			Faradays	Faradays/ Mole TKN Removed	Total Power Consummed (WH)	Pounds of Product Water Recovered	Watt hours/lb Product	Total Dissolved Solids in Pretreated Urine (ppm)	Electrodialysis				Total Watt hr/lb Product Water
		lbs run	24 hour Rate (lb/day)	Initial (g)	Final (g)	Removed (g)							Final Conductivity of Product Water (μ mhos/cm)	Final T. D. S. (ppm)	Total Power Consummed (WH)	% Product Water Recovered from E. D. Treat.	
5	12.0	6.7	13.4	22.56	1.68	20.88	13.4	8.97	1046	6.6	158		480	2500	86	85	202
6	10.0	6.7	16.1	22.35	2.31	20.04	11.2	7.76	863	6.6	131	24900	480	680(1)	152	84	183
7	8.25	6.7	19.5	19.20	2.14	17.06	8.8	7.24	690	6.6	104	23580	100	440(2)	36	96	110
8	9.0	6.7	17.9	19.32	2.77	16.55	9.3	7.86	747	6.6	113	26900	325	3400	138	81	165
9	11.0	6.7	14.6	22.26	2.10	20.16	11.4	7.95	875	6.6	129	23340	300	2400	132	82	186
Averages		6.7	16.3	21.14	2.20	18.94		7.95		6.6	127						

(1) Polished with 100 g/l of charcoal (Nuchar) after Electrodialysis

(2) Polished with 100 g/l of charcoal (Nuchar) before Electrodialysis

consumption was also measured and divided by the quantity of product water to yield a power factor, average value 127 WH/lb of product water.

The product of the electrolytic pretreatment cell was subsequently passed through the electrodialysis stack. The total dissolved solids was reduced from approximately 25,000 ppm to 2500 ppm in the electrodialysis stack. The solution conductivity of the diluent product of the electrodialysis stack was 500 micromhos/cm. This corresponds to approximately 500 ppm of inorganic residue. Thus the majority of the solid residue in the final product water is some form of organic material. The total solid content of the product water can be easily reduced to less than 500 ppm by simple contact with activated charcoal.

The presence of this dissolved organic solid increased the stack resistance and reduced its efficiency. This took the form of reduced current flow at the recommended operating voltage and increased processing time, see Table XVIII.

TABLE XVIII

ELECTRODIALYSIS STACK OPERATION

	Current* (amperes)	Time Required to Remove 16,000 ppm salt (minutes)
Before charcoal polishing	0.28	195
After charcoal polishing	0.71	40

*Voltage: 25 v
Solution concentration: 2700 μmhos/cm
~2000 ppm salts

This increased operation time not only increased the power required to remove inorganic salts, but it also increased the water loss in the concentrate stream. In fact the only measurable water loss occurred in this portion of the urine treatment. Because of this water loss the power required per pound of product water contribution of the electrodialysis treatment was much greater than the actual power required for the salt removal.

The effect of charcoal polishing is also illustrated in Table XVII. Product water from run 6 was polished with charcoal after electrodialysis treatment. In run 7 the charcoal polishing preceded the electrodialysis treatment. The improved electrodialysis performance may be seen in the lower power requirements and higher water recovery (95.5%) found in this run.

The dissolved solids remaining in the product water after the electrodialysis treatment are primarily organic since the final solution conductivity value of <500 μmhos/cm indicates an inorganic salt level of <500 ppm.

CONCLUSIONS

The design and process criteria of the electrochemical pretreatment of urine using Astropower catalyst were developed to the extent that the following results were achieved:

1. The average power requirement in the five-day test for pretreating raw urine was 127 watthours per pound of product water. This water contained less than 0.5 g of urea per liter and other organic materials. Power requirements increase rapidly as the removal of organics reaches completion.
2. The organics remaining in the urine after the pretreatment can and must be removed before electrodialysis processing to give a product water containing less than 500 ppm total dissolved solids and a water recovery of over 94%. Electrodialysis treatment with unpolished pretreated urine gave water recoveries as low as 81%. Polishing of the pretreated urine can be accomplished by charcoal adsorption.
3. No bacteria were found in samples of pretreated urine at the end of the five-day test. No effort was made to maintain a sterile system, therefore, the process is self-sterilizing.
4. No measurable water loss occurred in the electrolytic pretreatment process.
5. A Mark III cell was designed, fabricated and operated for five days at an average capacity of sixteen pounds of raw urine per day. The cell design incorporated stainless steel cathodes, platinum anodes, porous separators and open screen spacers. No loss of cell efficiency was detected over a period of one month of intermittent operation. No electrode deterioration was noted at the end of the five day test.
6. A critical cell operating voltage was established as 2.9 volts with the Mark III cell. Above this value performance was markedly improved.
7. The pretreatment process produces hydrogen and nitrogen in a ratio of 3 to 1 which is the theoretical ratio for the electrochemical oxidation of urea. The on-board use of these gases would reduce the weight penalty for using the process.
8. Rapid gas-liquid separation appears to be an important requirement to obtain low power processing. Porous separators were introduced into the Mark III design to prevent mixing of electrode stream products. Further investigation of the use of separators is required to establish their importance and function.
9. The pretreatment process operated successfully at ambient temperature.

10. Astropower catalyst has an accelerating effect on the electrochemical reaction. Astropower catalyst #7765 increases the rate of nitrogen removal by a factor of 4 to 5. Although the power efficiency is not significantly affected, lower voltages can be used to complete the processing within the requisite time.

11. It was also noted that hydrogen ion concentration is an important rate determining factor. Within the pH range 4.5 to 6.5 the rate of the reaction increases with pH, doubling between a pH of 5 and 6.5. During pretreatment the pH gradually falls and some adjustment is required.

12. Indications of the completion of the electrochemical oxidation are a rise in pH and the presence of oxygen in the product gas stream.

REFERENCES

1. Popma, D. C.; and Collins, V. G.: Space Vehicle Water Reclamation Systems – A Status Report. Chemical Engineering Progress Symposium Series, vol. 62, no. 63, 1966.

2. Everett, Jr., R.; Meier, E.; Odian, G.; Henley, E.; and Katz, A.: Water Recovery Study. NASA Report W 64 29503, Radiations Applications, Inc., Long Island City, N. Y., April 1964.

3. Pucknat, A.; Scardaville, P.; Tuwiner, S. B.; and Wetherall, T.: Water Recovery Study, Electrolytic Purification of Urine. NASA Report N65-34973, Radiations Applications, Inc., Long Island City, N. Y., November 1964.

4. Tuwiner, S. B.: Research, Design, and Development of an Improved Water Reclamation System for Manned Space Vehicles. NASA Report CR-66323, RAI Research Corporation, Long Island City, N. Y., April 1966.

5. Standard Methods for the Examination of Water and Waste Water. American Public Health Association, 11th ed., 1960, New York.

6. Hawk, P. B.; Oser, B. L.; and Summerson, W. H.: Practical Physiological Chemistry. McGraw-Hill Book Co., Inc., 1954.